A COMPARATIVE STUDY OF DETERGENTS

WITH SPECIAL REFERENCE TO THE TEACHING OF THE SUBJECT

By

ELLEN BEERS McGOWAN

L. Ed.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PHILOSOPHY, COLUMBIA UNIVERSITY

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E. B. M.

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A COMPARATIVE STUDY OF DETERGENTS

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INTRODUCTION

Purpose and Scope of Study

The purpose of this study of products which are of daily importance in the life of every individual, is to meet certain needs of the consumer with relation to these products, primarily through the school. It is not the aim of the study to make a contribution to the large amount of technical information available concerning soaps and other detergents. A great deal of research has been conducted, and is constantly being pursued, in this field, but much of it is too technical and abstract to be of value to the consumer, except indirectly as it results in the manufacture of new and improved products. Even these, in their multiplicity, create a difficulty for the average purchaser, upon whom is laid the burden of responsibility for choice and use, at a time when fashions in materials are creating an obligation for greater discrimination in choice and more intelligence in the use of detergents.

Approximately eighty per cent of the general and personal laundry of the American family is still done in the home; therefore the problem of detergents is a real one for the great majority of homemakers. Although the average homemaker knows less about modern detergents than did her mother or grandmother about the relatively few soaps in their day, she must deal with textiles of a delicacy unknown to the laundry of an earlier time.

Consumer's Need to Know How to Choose and Use Detergents

Intelligent choice is important, for it is almost as much of a fallacy to say that any given soap is equally suitable for the roughest cleaning and the finest fabric, as to say that the diet of a lumberman is suited to the infant. In the first case the effects are

usually less tangible and immediate, that is all. In *Hotel Soaps and Cleaning Compounds,* a pamphlet prepared by the Research Bureau of the American Hotel Association, the statement is made that "countless instances of damage to fabrics, marbles, paint, nickel, etc., caused by using the wrong cleansing agent or an impure article, have been related to the persons who compiled the material in this manual."

From the standpoint of cash expenditure, it may not be significant to say that the average American family uses about one hundred and fifty pounds of soap products yearly. This is a conservative estimate. A large percentage of soap consumption is accounted for by various commercial industries, but the Bureau of the Census reported about three billion pounds of soap products manufactured in the United States in 1927. This amount represented the output of 256 soap manufacturers, whereas it is estimated that about 700 manufacturers should report. That our soap business is of huge proportions is obvious. A statement has been made that if all America washed its hands once more daily than its present habit, the consumption of soap would increase by about 400,000,000 pounds yearly.

Granted that fifteen dollars per year is an average expenditure for detergents per family of five. If knowledge does not stand behind the choice and use of these detergents, who can measure the possible depreciation in wearing apparel and household belongings due to incorrect usage? This is the economic consideration to keep in mind—not what soap products *do* cost, but what they *may cost.*

The last twenty years have seen great changes in the number and form of detergents on the market. Up to the present century the bulk of the soap manufactured in this country was in the form of bars. There was no great range of choice; a few standard bar soaps were household favorites, and the cotton articles of the typical family wash were rubbed with these soaps, scrubbed on the washboard, and usually boiled.

Then came the general use of silk for stockings, lingerie, and other washable articles. Immediately a mild soap was required, in a form adapted to rapid solution. A new type of soap, in flake form, consequently appeared, and new methods of laundering emerged. This demand for special soaps has steadily increased, for silk, wool, and rayon or synthetic fabrics are in

universal daily use. They are comparatively expensive, and since they need gentle treatment in laundering, they are usually washed by the wearer. The swing of fashion from befurbelowed dresses to simpler styles has also increased the laundering of outer garments which formerly have gone to the dry-cleaner.

About the time that these changes in women's dresses were beginning to revolutionize the soap market, the mechanical washing machine came into the home, to do away with the washboard and to create a demand for a soap for general laundry purposes which would go into quick solution before the clothes entered the machine. Thus attention became centered upon the correct laundry principle of dissolving flaked or chipped soap before beginning the washing process, rather than rubbing soap on the garment. Consequently the consumption of bar soaps for laundry purposes has greatly declined, and all these influences have combined to bring upon the market a host of new forms. We still have soaps in bars, but also in flakes, chips, powders, grains, beads, pastes, tablets, and liquids. And there are a number of other detergents advertised for laundry or other purposes, which are not soaps at all.

Here, then, is a problem which has sprung up overnight, as it were. This problem of choice in an almost unlimited range of offerings involves economy, efficiency, and fabric safety. From what sources shall the average consumer get the needed information regarding choice and use? Does advertising give it to her?

To What Extent Is Advertising Helpful?

The bulk of soap advertising is not educational. In so far as certain well known and reliable soap manufacturers are concerned, the advertising of the staple products with which their names are associated is quite generally done in a spirit of scientific progressiveness, with an appeal to the intelligence of the consumer. Yet even with these makers of intrinsically good products, competition creates the pressure to capture a wide market, a pressure which swings the trend of their advertising toward recommending more universal uses for certain products than is sometimes justified. If this pressure of competition is felt by the leaders in the industry, how much more does it affect the manufacturer of one or two specialties, who feels that he must ascribe magical powers to his products in order to capture the attention of the buying

public? Unfortunately there is something convincing merely in the printed word, and the hundreds of specialties which are on the market testify to the appeal of advertising.

Much that is done in the name of advertising is based solely upon the power of suggestion, and is an affront to the intelligence of the consumer. The wildest claims are hopefully accepted by the incurably optimistic and uninformed purchaser. She believes in a product which advertises itself to be equally good for shampooing and for washing greasy pots and pans; for the personal bath and as a stain remover; for washing silks and woolens and for the general laundry. Thousands of consumers do not understand why such contradictory claims cannot truthfully be made for any detergent.

The consumer is entitled to know the truth about the product her money buys. Honest, conservative statements would in most cases win her attention and confidence, and react favorably for the manufacturer. It is time that advertising had a scientific as well as a psychological appeal, in this as well as every other household commodity.

But there must be reciprocity. More intelligence on the part of the consumer is needed. It is significant that several pamphlets and series of talks on scientific washing and the conservation of textiles are in circulation among commercial laundries, which are unknown to the homemaker, but which would be of great educational value to her if she were ready to appreciate them.

Justification for Study of Detergents in School

It would be pleasant, if it were possible, to gather in a little handbook for the consumer the pertinent facts about the whole problem of detergency as met in the modern home, but it is difficult to make a true and complete picture of the properties and behavior of chemical substances such as soaps, without bringing in terms and concepts beyond the comprehension of those who have no elementary knowledge of the chemistry of detergents. It is here that the school has the opportunity to bridge the gap between technicalities and practice. Nor is it necessary to wait for high-school age in order to do this. In the elementary grades, children develop scientific-mindedness, and show an appreciative understanding of simple chemical facts. Why not enter with easy

steps into a field of chemistry so closely touching their daily activities? The field will not shrink in value as the comprehension of the child increases; there is ample scope for research in it in the university, and abundant material for the years between.

If soap is a necessity in effecting cleanliness of body and clothing, if it promotes health and aids in the prevention of disease, is it not a worthy topic for the curriculum? If some knowledge of what soap is, how it performs its cleansing action, why certain types of detergents are better than others for given purposes, is a valuable part of the equipment of a homemaker, is there not an obligation laid upon a school which believes in training for everyday living, to incorporate the necessary knowledges in its curriculum in order that they may function in the home?

This is the purpose of this study: To present these knowledges simply yet scientifically, that the whole may be a guide or source book for the teacher or the consumer. It is hoped that the teacher may find in it selective material for different ages and inspiration to further study in the advanced grades.

For many of the facts incorporated in this study the author is indebted to a long list of books and periodicals, some of which are included in the bibliography. Experiments conducted over a number of years in the Household Chemistry laboratory of Teachers College, Columbia University, have furnished the information for the practical evaluation of soap products and their uses.

CHAPTER I

DIRT

Definition

A considerable part of the time of the world is spent in removing dirt. Dirt has been inclusively defined as matter out of place. The nature of such matter should be briefly considered, before studying the detergent remover, the method of removal, and the interrelation of the textile fibers with both dirt and detergent in the achievement of cleanliness.

Classification

Dirt may be roughly classified as follows:

Water-soluble dirt.
Dirt insoluble in water.
Stains.

Water-soluble dirt is seldom found apart from insoluble forms. Soluble foodstuffs such as sugars, or soluble acids and alkalies acquired from foods, body contacts, or from materials in the environment, are often admixed with less soluble coloring matter or with grease and dust. Nevertheless, although it seldom happens that water alone is an adequate detergent, it should be the first resource whenever it can be used at all. Prompt treatment of a spot with water alone is often sufficient to prevent concentration of the foreign substance and harmful chemical combination with the textile material.

Description of Removal Methods

Too much emphasis cannot be placed upon the necessity of prompt removal of this form of dirt, or indeed of dirt of any kind. Acids and alkalies attack textile fibers in varying degrees, and cause deterioration. The perspiration of the body is usually acid in character at first, but may become alkaline by decomposition. Experiments conducted in the Household Chemistry laboratory in Teachers College have shown that alkaline perspiration is especially harmful to many delicate colors and fabrics. Further-

more, soiled places in clothing continue to grow more soiled by attracting grease and dust; stains may become fixed by oxidation or chemical combination with the fiber; penetration into the fiber cells themselves may be progressive; and not least of the reasons for prompt treatment of dirt,—it invites bacteria.

Removal of Soluble and Insoluble Dirt

Dirt may be either soluble or insoluble. Dirt insoluble in water requires either a solvent or an emulsifying agent, or both, for its removal. Soap is a universal detergent because, generally speaking, it is both solvent and emulsive in its action. It extends the solvent action of water, and is one of the best known emulsifying agents for enclosing and floating off particles of grease and dust. Fats and oils of all kinds, paint, resinous or gummy substances, many proteins, gritty substances and dust, are included in the list of insoluble forms of dirt, but the most common and troublesome of these are the fatty substances. No clothing is free from grease of some kind very long; body contacts, foods, even the air of thickly settled communities, offer too many chances for contamination.

If grease spots are not promptly and thoroughly removed, they may oxidize to substances which are as difficult to remove with ordinary cleansers as a coat of varnish, because they pass through the same kind of oxidative change that varnish does in hardening. That is, by the action of the oxygen of the air on any unsaturated fatty acids in the oil or fat causing the grease spot, there is formed a product which dries to an impervious film in the fabric, exactly as a similar change takes place in the linseed or other unsaturated oil in a paint or varnish. And again, grease spots are areas attractive to bacteria and moths.

Dust in clothing acts much as would abrasive or emery paper, if it is present in the portions of a garment exposed to friction; and if not removed plays a considerable part in the wear and tear on a fabric.

To what extent these soluble and insoluble forms of dirt actually penetrate the fiber walls and enter the cell structure of the fibers which compose our fabrics; to what extent detergent solutions are able to follow dirt into the fiber body and there combat and remove it, and the effect upon the textile fibers of both dirt and detergent, are subjects discussed in Chapter II.

Removal of Stains

There remains to be mentioned this class of dirt, stains, the removal of which is a constant household problem. Stains are too varied, and their treatment too specific, for full consideration here, but emphasis may be given to those which may be removed, or remedied, by water alone or by a soap detergent.

A stain is a form of dirt which carries color but which does not immediately, at least, fix that color permanently upon the fabric. Color fixed more or less permanently is a dye rather than a stain. Prompt treatment of a stain often prevents it from becoming a dye by physical or chemical change.

Before any stain is treated, three things should be known: the stain, the fabric, the effect of the proposed treatment upon both stain and fabric.

Since water alone, cold or hot, is for most stains the least harmful of preliminary treatments, it is the first thought in the majority of cases. There is a saying that all water-borne stains must be removed by water. Cold water put upon a stain at the time it occurs will make its complete removal later an easier operation. Hot water must not be used on such stains as blood, egg, or milk, since the protein they contain is thereby coagulated in the fiber.

It is well to have in mind the stains upon which water alone, water and soap, or other simple treatments with detergents such as borax or ammonia, will be effective.

Sugar, starches, milk, vegetable stains, blood, fresh mildew, bluing, ice cream, albumin, perspiration, fresh tea or coffee stains, scorch on cotton and linen, and fresh grass stains are more or less completely removed by cool water. Boiling water is effective on fruit stains and also on tea or coffee stains if not mixed with milk or cream. Dye stains frequently disappear with boiling water.

As a rule, the plain water treatment for the above stains should precede a soap treatment. There are definite reasons for this in the case of blood, tea and coffee, and some fruits. Where iron is present, as in blood, an immediate application of an alkali such as soap forms an insoluble iron compound which leaves a yellow stain. This stain can be removed with oxalic acid. Oxidizing bleaches such as Javelle water or a chlorine bleach in general are not so effective as they increase the oxidation of the iron to the insoluble form. In the case of tea, and to some extent coffee, the

presence of tannin may cause a stain to appear with soap. Tea stains are still further complicated by a coloring matter. Glycerin is usually effective in removing a stain residue after a water treatment of tea and coffee spots, if the spot is of long standing. Tannin in certain fruits, as well as acid constituents which make combinations with alkalies, make it unwise to rub soap directly upon most fruit stains, although a soap solution following a plain water treatment is sometimes an effective remover.

Acid spots result frequently from chemicals used in electrical batteries, etc. They must have prompt neutralization with soap solutions, ammonia, borax, or washing soda, the choice of these depending upon the color and nature of the material.

Soap and water are effective in the long list of spots from various greases, fresh paint, stove polish, machine oil, crank-case oil, and tar (with lard first, then soap and water). If the garment cannot be treated with soap and water a grease solvent such as carbon tetrachloride must be used, but the commercial dry-cleaner finds such solvents more effective if combined with soap.

The method of wet brushing with water or soap solution is convenient in case the entire garment cannot be washed. For this the article is brushed dry, laid on a table, padded with cloths to absorb water, and quickly brushed with a soap solution followed by a clear water brushing and drying.

A good procedure in the removal of any stain is as follows:

1. Place the garment on a clean table.
2. Isolate the spot as completely as possible.
3. Cover remainder of garment with a protecting cloth.
4. Place folded cloth or white blotting paper under the spot, and change frequently during the removal treatment. The stained area may be stretched over a bowl. Use the cloth for unwashable goods and the bowl for washable.
5. Many short applications of the stain remover, followed by neutralizations if an acid or alkali is being used, are less harmful to the fabric than a long continued treatment.
6. Beware of inflammable grease solvents. Friction alone may ignite such.
7. Neutralize acid stains with mild alkalies such as dilute ammonia, soap, or borax solutions. Neutralize spots of alkali with a mild acid such as vinegar.
8. Do not leave traces of the stain remover in the fabric after the stain is removed. This is a necessary caution in the use of acids and alkalies.
9. If rings form, steam or brush to remove.

Clothing which can be starched slightly is protected to some degree from the ingraining of soil and stains. But starch inter-

feres with the absorptive capacity of material, and should not be applied to toweling or to clothing worn next to the body.

The more specific action of stains and removers upon the fibers is discussed in the following chapter.

CHAPTER II

THE TEXTILE FIBERS

Necessity for Knowledge of Textiles

The commercial laundry has been notably progressive in recent years with regard to the conservation and scientific laundering of textiles. Conservation of textiles is the watchword of the better type of laundry, and through the Laundryowners' National Association there are maintained fellowships for research in the nature and properties of the textile fibers, as these are related to the laundry problem. The result is that the members of the Association have available information of great value concerning many phases of the whole problem—the nature of the textile fibers, the nature of detergents and their effects, and proper methods of water softening, control of temperature, bleaching—all of which makes the difference between a laundry conducted on scientific principles and one run by guesswork.

Much of this knowledge should be part of the equipment of every woman, for as has been said, in spite of the improved service offered by the commercial laundry, more laundering is done in the American home than out of it. Materials for personal wear, particularly silk and rayon, wool for hosiery and sport clothes, and bright-colored fabrics, are usually washed at home. These are the fabrics which need special care, yet the home laundress has not progressed as fast as the commercial institution in the scientific understanding of the nature and care of textile material.

Cleansing of Five Major Textile Materials

In spite of the marvelous variety of fabrics, there are only five major kinds of textile material. The fact that there are only five simplifies the problem. There are wool and silk from animal sources, cotton and linen of natural vegetable origin, and the synthetic fibers, also of vegetable origin. These synthetic fibers are sometimes called rayon, but are distinguished as viscose,

cuprammonium, cellulose acetate, and nitrocellulose filaments, according to the process of manufacture.

The animal, the vegetable, and the synthetic fibers have their peculiar properties which must be taken into account in the cleansing operation, in determining detergent and method to be used.

Wool

Wool is the greatest collector of surface dirt, and the most difficult to cleanse. Much of this is understandable when the wool fiber is examined under a microscope. Its natural crimpiness, and the presence of scales with protruding edges, present innumerable points of attachment for dirt.

The difficulty in laundering wool is caused by both physical and chemical characteristics. Both the soap and the method must be chosen with care.

Wool, as an animal fiber, is a protein, belonging to the general group of proteins in which the hair of our heads, the skin, the finger nails, and gelatin as a derived form are found. As is more or less characteristic of this group of proteins, wool, insoluble in cool water, swells and becomes plastic to a certain extent in hot water. In fact, if wool is boiled for any length of time, some of it goes into solution in a manner similar to its related substance,—gelatin. From the laundry standpoint, the important fact is not its behavior in boiling water, for it is generally known that wool should not be boiled, but *its tendency to become plastic* in hot water, with results which will be noted later.

Hot water does more than produce plasticity of the wool fiber. It is a tremendous accelerator of chemical action. As the temperature of a water solution of acids or alkalies increases, so does their chemical activity. For example, a piece of wool material might lie in a cold solution of sodium hydroxide or caustic soda for a half-hour without visible deterioration, whereas the same solution at 150 degrees Fahrenheit or more will dissolve it in a very few minutes.

Being a protein, wool is both acid and basic in its nature, but it appears that the basic nature predominates; for it can neutralize to a degree acids with which it comes in contact, whereas its inability to neutralize bases to a protective extent results in a greater susceptibility to the action of alkalies than is found in any

other fiber. This fact makes the choice of soaps having a strong alkaline reaction as unwise for the washing of woolens as for shampooing the hair. Even the mildest soap becomes somewhat alkaline in water solution, therefore to conserve the strength of wool fabrics the soap should not only be mild, but the activity of the alkali should not be increased by hot water. Water at approximately body heat will allow body oils to remain fluid and in a condition for emulsification and removal by soap.

Occasionally we read a recommendation that a little soap be left in the rinse water, in washing blankets and wool sweaters or such articles, for the sake of a soft feel in the garment. The argument against this practice is that it can be demonstrated by chemical measurements that wool absorbs alkali from a soap solution, and unless the material is thoroughly rinsed the solution concentrates in the fiber on drying. Here it remains as a menace to the strength of the material.

In speaking of the alkalinity of soap in solution, the usual alkali in question is the sodium hydroxide which entered into the composition of the soap, and which the water has re-created to some extent. Other alkalies are often added to soaps, such as washing soda, borax, and sodium silicate. These are milder in chemical action, and may restrain the action of the sodium hydroxide; nevertheless they are alkaline. Their purposes and values in soaps are discussed in the chapter on Soap Additions which includes a discussion of "builders."

So much for the chemical effect of hot water and alkalies on the wool fiber. There is a physical effect which is as distressing as the chemical. Shrinkage of the fabric, even to a hard, board-like material, may result from a combination of hot water, strong soap, and especially a wrong method of handling. The trouble starts with the hot water in making the fibers plastic. Alkalies increase this softening effect. Then if friction—rubbing or wringing—is applied there is fusion of the plastic fibers which mats the mass, contracts it, and causes permanent shrinkage. Although their effect is minimized by some authorities the epidermal scales evidently have some part in the shrinkage of wool, by interlocking of protruding edges. The proof of this effect seems to be that hair fibers, which come from goats rather than sheep, but are chemically similar to wool, have scales which are barely perceptible, being held closely to the body of the fiber without protruding

edges; and fabrics made of hair fibers, such as mohair fabrics, are much less susceptible to shrinkage.

Therefore to remove dirt from wool successfully, the soap must be mild or so-called neutral, the temperature no higher than that required to keep grease or oils in the fluid state (body temperature suffices in most cases), no rubbing or twisting must be done, and the temperature of the rinse waters must be uniform with the wash water, for a change to cool water will contract and still further felt the softened fibers. If the article is quite soiled, it is well to follow the first wash water with a second, using good suds in both, in order to float off more thoroughly all entangled dirt particles. Extra full suds are necessary in washing wool fabrics, because the air spaces in the fibers seem to entangle and break down the suds.

Wool is affected by dry heat in much the same way that an egg is affected by cooking. For instance, if a dampened wool fabric is suddenly dried by too hot an iron the fibers become hard and brittle, nor is the softness and elasticity ever regained.

Silk

Silk is a naturally clean filament. Its difference from wool in this respect is inherent in the smoothness and straightness of the fiber, which is so long by nature that a fabric made from reeled silk does not have many protruding ends to catch dirt. On the contrary, spun silk material often shows fuzzy ends, because it is made of short lengths of silk from pierced cocoons or machine wastes, spun and twisted like cotton.

As silk is produced by the silkworm, it consists of two proteins, one of which, the sericin or silk glue, is soluble in hot water, and is removed in one of the preparatory processes of silk manufacture if a so-called "bright" silk is desired. The other protein is fibroin, which is insoluble in cool water, and less susceptible to hot water than is wool. Neither is silk so quickly deteriorated by alkalies as wool, although it stands next among the textile fibers in degree of susceptibility. It appears that silk is slightly more acid in character than wool, since it cannot withstand the action of most acids, yet more slowly succumbs to alkalies.

Because of the delicacy and the cost of silk, careful washing is needful. Rubbing and twisting are harmful, because silk is slightly weaker wet than dry, and moreover its straight, smooth

filaments do not adhere in the weave as well as crimpy wool or curly cotton fibers, so that there is a tendency in looser weaves to slip out of place with friction. In regard to soap and temperature, the same rules hold for silk as for wool. So much silk is used for knit goods, in stockings and lingerie, where softness and elasticity are necessary for long wear and the prevention of "runs," that for these fabrics the mildest of soaps, which will conserve these properties, are especially necessary.

Dry heat is even more destructive to silk than to wool, partly because its filament is more delicate, without the horny scale protection. A temperature of 200° F. is dangerous to silk.

Synthetic Fibers

Synthetic fibers have many admirable qualities. They do not attract dirt, because of their smooth, long filaments; dirt and most stains wash out easily; white rayon does not become yellowed with wear as white silk does; they are not as susceptible as silk to the action of alkalies.

These synthetic fibers are not artificial silk; they are not intended to take the place of silk, and therefore should not suffer derogatory comparison with silk. As a class, they have become the fifth major textile fiber, but in wide adaptations to many uses, they stand first in rank.

The term "rayon" has been proposed for these fibers, but if used it should be qualified so that it is clear which one of the four principal types is meant. These types differ as to processes of manufacture, and naturally differ somewhat in physical and chemical properties. They lose their identity as rayon unless we specify cuprammonium rayon, such as Bemberg; cellulose acetate rayon, such as Celanese; nitrocellulose rayon such as Tubize, and viscose rayon such as Viscose or Glanzstoff. The student of textiles recognizes differences in these, but the wearer must keep in mind one property which all hold in common in different degrees —the property of losing strength when wet. This loss of strength may be as high as forty to sixty per cent of the strength when dry, but it is regained on drying. Some synthetic fabrics have a high initial strength, in which case it is often found that when wet they still are stronger than many materials made from other fibers. But some, on the other hand, lack this initial strength, so that their increased weakness when wet makes it possible to break the

fabrics with a slight twist or pressure. Therefore, while mild soap and moderate temperature are desirable, the main thought in washing rayons is gentle handling without any friction while wet, and drying without strain, either of clothespin pressure or the weight of the suspended fabrics on the clothesline.

Improvements are being made in synthetic filaments with regard to this loss of strength while wet, and certain kinds with great initial strength are superior in this respect to the degree that stockings and lingerie of this kind have been proved to outwear silk stockings and lingerie of much greater cost.

There is some stiffness and lack of elasticity in a new rayon stocking which prevents the close-fitting effect of silk, but this more or less disappears after the first or second washing.

Admixture with other fibers is of frequent occurrence, in which rayon adds interest and beauty to the fabric, and receives strength itself. Such mixtures should still be considered as rayon articles in washing. A woven rayon is like silk in that the threads may slip if rubbed, because the smooth filaments of both lack the property of adhesion.

Cotton and Linen Fibers

Cotton and linen fibers may be compared in much the same way as silk and wool. That is, the linen fiber is straight and smooth; the cotton fiber in its natural form is twisted, almost curly. Because of this difference in structure, dirt and bacteria have been found to attach to cotton to a greater degree than to linen, in comparable weaves, and to be correspondingly more difficult to remove. The longer fiber of good linen in a fabric, also prevents the protrusion of the fuzzy ends that are seldom absent with the short-stapled cotton. Mercerized cotton, however, which has lost most of its curl and gained smoothness in the process of mercerization, resembles silk and linen in its greater cleanliness.

Cotton and linen, being vegetable fibers, belong to the carbohydrate group of chemical substances. Both are practically a pure form of cellulose after being freed from impurities and fully bleached. Celluloses are as a class inert substances toward neutral solvents, and are not so susceptible to the action of alkalies as to acids. Strong acids have a tendering effect on cotton and linen, but alkalies, except under certain conditions, may be used upon both with impunity.

In both commercial and home laundering it is customary to use stronger detergents for cottons and linens than for silk, wool, and rayon. If the method is correct, the practice is justified, except perhaps for the more delicate fabrics. Alkalies do have a chemical action on vegetable fibers, but again the action is so controlled by temperature, that the same solution of sodium hydroxide which will mercerize and strengthen cotton *in the cold*, will at the *boiling temperature* slowly change it to brittle oxycellulose, in the presence of air. Air is present in ordinary washing operations. Cotton boiled in dilute solutions of sodium hydroxide may lose five per cent or more strength. (Heuser: *Textbook of Cellulose Chemistry.*) This action of hot alkalies points to a good rule for the home laundry: That cottons and linens should not be regularly boiled in an open boiler with strong soaps or other alkalies, except for purposes of sterilization. This is not a consideration under ordinary conditions, where no contagious disease is present, yet many laundresses believe firmly in the old-fashioned boiler on washdays. The best temperatures for washing cottons as well as other materials are summed up in Chapter VII.

Over-bleaching of cottons and linens with oxidizing bleaches such as Javelle water, hydrogen peroxide, or perborates, will also form oxycellulose, especially if some bleach is left in the material. White cottons such as bath towels are sometimes over-bleached in laundries and have an over-white appearance and a harsh and brittle feel. They soon fall in pieces when this stage is reached.

The constant use of a bleach achieves whiteness at the expense of strength. All bleaching involves chemical action on the coloring matter in the fiber and to a certain extent on the fiber itself. The case of linen is well known. Unbleached linen is so much stronger than the same linen full-bleached that the latter has been estimated to have lost, on an average, twenty-five per cent of its strength. Even sun bleaching, where no chemicals are used, pulls down the strength of linen as much as twenty per cent. All housewives know that almost any curtain material becomes tender on long exposure to sunlight. Oxycellulose is the product formed in vegetable material, and an oxidation product results in silk and wool which is also a disintegrative change. Bleaching is not necessary as a weekly laundry operation in the household, when a good soap is used and the article is thoroughly washed and equally thoroughly rinsed.

Fiber Penetrability

But the question of dirt removal involves more than the chemical reactions of a fiber or its outer surface. Those fibers which are the result of a natural process of growth, such as the wool of the sheep and the cotton and linen fibers, have a cell structure which underlies the outer covering. They also have a more or less pronounced central canal or medulla running through the fiber. Silk, however, the result of the hardening of a continuous stream of protoplasm from the spinning organs of the silkworm, is not built up by definite cell growth, nor would it have the central canal which is the avenue of nutriment for the wool, cotton, and linen fibers. Rayon and silk are similar in this general structure.

In the case of fibers having a central canal, this canal is outside the fiber in the sense that the alimentary canal is outside the body. That is, it is penetrable by all kinds of dirt, being open at least at one end. While it makes a decided problem in dirt removal, it is not the same problem as that created by the penetration of some kinds of dirt into the real body of the fiber, or fiber cells, of wool, cotton, and linen, or the inner part of the silk and rayon filaments.

Personal Investigation to Determine Fiber Penetrability

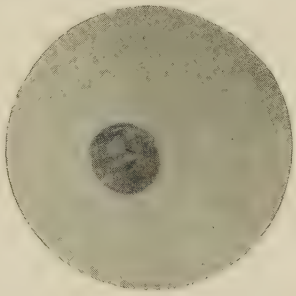
A personal investigation to determine fiber penetrability was conducted. How far does water-insoluble dirt, such as fats and oils, penetrate into the body of the fiber? Are some fibers non-penetrable, while others are freely so? If fats do penetrate, do soaps enter the fiber body and remove the fat? Do other detergents enter equally well?

In an endeavor to answer these questions, a study was made of the penetrability of water-insoluble substances such as fats into the fiber cells of wool, cotton, and linen, and into the body of the silk and rayon filaments.

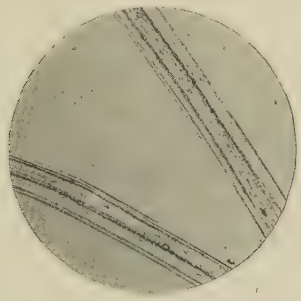
The following method was used: Wool, silk, cotton, and linen fibers, and the four leading kinds of rayon, were washed free from natural fats, and immersed for twenty-four hours in lard, and cottonseed, olive and coconut oils in an incubator at a temperature of 125° F. They were then washed free from surface fat in warm absolute alcohol, dried, and soaked in osmic acid for twenty-four hours. Osmic acid turns fat dark gray or black. At the same time controls were set up corresponding to the test fibers,

each set being immersed in osmic acid without having been previously soaked in the fats. The fibers were then embedded and cross-sectioned in the usual way, and studied under high magnification, both longitudinally and in cross-section. The control fibers were in all cases free from fat both within and without the fiber, as shown by the lack of response to osmic acid.

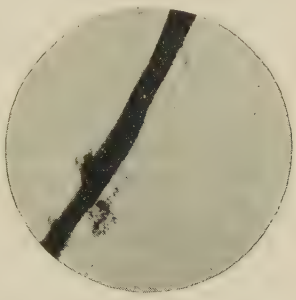
Cross-section of Flax Fiber stained with Osmic Acid (x460)



Cross-section of Flax Fiber stained with Osmic Acid (x1160)



Synthetic Fibers with Absorbed Fat stained with Osmic Acid (x460)



Flax Fiber showing penetration of Fat (x300)

The tests established certain facts:

That fats penetrate vegetable fibers of all kinds, but in the tests made they showed slight or no penetration of animal fibers, i.e. wool and silk.

That the rayon filaments as a class allowed less penetration than cotton and linen.

That lard, an animal fat, showed a greater degree of penetration than the vegetable oils, in the scope of the tests made.

That a most thorough cleansing is necessary to free from fat those fibers which have an open medulla.

The second part of the problem undertook to determine the value of certain detergents in removing fat from the body of the fiber, after penetration.

The detergents used were (1) a pure soap; (2) a soap containing washing soda; (3) washing soda alone; (4) carbon tetrachloride; (5) cleaning naphtha or gasoline. The method included the preparation of the vegetable fibers as before. After the fat had penetrated the fiber body, the surface fat was removed, and the fibers immersed in the respective detergents. The soap and washing soda solutions were of one-half of one per cent strength. At the end of an hour's immersion the fibers were agitated, removed, dried, and soaked in osmic acid for twenty-four hours. Cross-sectioning gave the following data:

The two soaps used removed all the fat.

Carbon tetrachloride removed nearly all, but some staining with osmic acid was seen.

Washing soda and cleaning naphtha left most of the fat in the intercellular spaces.

Some conclusions of practical import are:

That if a fat-spotted garment can be washed, it can be cleaned more thoroughly by washing than by dry-cleaning with a grease solvent; for soap and water treatment was effective in every case.

That if a garment is dry-cleaned, the recurrence of the grease spot, which is a common trouble, is due to the fact that the grease solvent removed only the surface grease.

That a combination of grease solvent and soap, such as may be found in some of the commercial grease solvents, is more efficacious than the former alone.

Paul C. Trimble, managing director of the National Association of Dyers and Cleaners, in a recent address said: "It is impossible for dry-cleaners to cleanse a garment properly without the use of soaps. Dry solvents, such as petroleum distillate, carbon tetrachloride, benzol, and camphene, all remove superficial soil without soap, but there is no good plant in the United States which does not use benzine-soluble soap in its processes and in large quantities."

There is no doubt that the greater efficiency of a soap solution in this grease removal from intercellular spaces is related to the colloidal nature of the soap solution, with its low surface tension, emulsifying power, and adsorption.

Cowdry, in his *General Cytology*, says that the permeability of the cell walls of living cells is related to the polar or non-polar character of the substance. In a fat, the polar bodies are the acid groups or residues, the non-polar, the remaining hydrocarbon chain. There may be differences not yet determined between the permeability of living and of dead cell tissue, as, for instance, the inert tissue of fibers after severance from the living source; but one fact stands out from the opinion of Cowdry—that fats which have aged and set free fatty acids are more permeable than "undissociated" fats. Therefore a grease spot just incurred is more easily removed than one which has lasted long enough to increase the permeability of the fatty matter by dissociation into fatty acids.

So it appears that the problem of thorough cleansing of the textile fibers with the least deteriorating effect is a complicated one, requiring special knowledge. Wool, cotton, and linen have their interior canals from which foreign substances must be removed; wool, silk, and rayons need special handling; cotton, linen, and rayons are penetrable by fats, and all fibers, naturally, are penetrable by water, which may carry with it water-soluble dirt. But what water can take in, water can take out, especially when aided by soap, so that we come back to the insoluble dirts and the stains as the real cleansing problems, to which must now be added the problem of colored fabrics.

Dyed Fabrics

How Color Complicates Cleansing Operations

Color complicates any cleansing operation. It is a rare dye which is fast under all circumstances, and to all influences. Washing, sunlight, weathering, acids and alkalies, bleaches, perspiration, are some of the hazards which dyes meet in the ordinary wear of clothing. Among so many dyes, of various classes, naturally some are better than others, and many which are fast to certain influences cannot reasonably be expected to be fast to others. The consumer should learn not to demand the

impossible from dyes, and should know that even when a dye is guaranteed to be fast to washing, a property in which she is most interested, the method of washing must be carefully controlled.

Because a dye is as fast as the dyer can make it is not a valid reason for concluding that its molecule cannot be dislodged from the fiber. Hot water causes expansion and loosening of dye molecules; friction helps to rub off surface molecules and change the color; strong alkalies may alter or fade certain dyes; the article may not only be carelessly washed but subjected to heat or sunshine during drying.

Colors can be obtained, often under a guarantee of fastness, which will endure a number of launderings or the usual amount of sun exposure, if they are washed in tepid water with a mild soap, handled quickly without undue friction, rinsed in cool waters, and dried away from direct sunlight or wrapped in muslin until ironed. If a color shows signs of streaking or running while being washed, the washing must be rapid, the rinsing done until no more color tinges the water, and the article dried quickly in a current of air away from sun or direct heat.

The Consumer's Responsibility

There are many ways in which a consumer can ensure the greatest economic return for her money, and her responsibility for this does not begin and end with a knowledge of the textile fibers and the best method of laundering them. It begins, and this in relation to the laundry, when she stands at the department store counter, and buys her wash goods. If she keeps washability in mind, she will remember:

Weave of Fabric

To consider the weave of the fabric. Long floats rub and break in the wash, and cause holes in the table damask; single threads of rayon or silk causing a novelty effect by overlaying a heavier thread soon wear away; heavy and light yarns alternating do not endure; corded effects against thin weaves in dimities, for example, soon cause splits along the cords; bath towels with a thin foundation are not worth the money paid for them; novelty weaves in general usually launder unsatisfactorily; allowance for shrinkage must be made when buying crêpe fabrics.

Fastness

To look for a guarantee of fastness when buying colored cottons or linens. Either the manufacturer's guarantee as a trademark, or the store's guarantee, is quite universally given in these days, and the consumer should be willing to pay the slight additional cost of the better dye and the protection.

Style of Garment

To consider the style of the garment. Not only cottons and linens, but rayons always, and wool and silk goods often, can be washed successfully if there is nothing about the fashion, as well as the color and weave of the garment, to create a problem. As has been shown, washing is more satisfactory than dry-cleaning, if the garment allows it, and the washer has the requisite knowledge and skill.

Accidents Which Befall Textile Material

The consumer is also responsible for some accidents that befall textile material, and which come out as sad defects when the article passes through the laundry. For instance, certain deodorants contain acids which destroy silk and may with careless use touch the wearer's silk lingerie; spilled medicines, cosmetics, storage battery acids, cigarette scorch are accidents that can be prevented by care and foresight. So also can the cutting of a hand towel by a razor edge, or a dish towel by the wiping of knives with edge toward the towel. And more damage to washable material is done by over-soiling than most people realize, not only by the chemical action of the soil but by the drastic treatment that such articles must have to make them clean again. Overbleaching and the careless removal of stains by chemicals are other common ways of shortening the life of fabrics. Very often the commercial laundry is blamed for the sudden deterioration of an article, whereas the blame rests on the consumer for any one or several of these ways in which she may have neglected her responsibility.

CHAPTER III

WATER

Solvent Powers of Water

In most households of the United States water is taken for granted and used abundantly without appreciation of its value. When something happens to curtail the supply, we realize the fundamental need for it in daily living.

Water is called the universal solvent, and there are very few things with which it comes in contact, that it does not dissolve to a greater or less degree.

But, though water may be a dirt remover by reason of its solvent power, this same power tends to dissolve substances which it meets, and sometimes complicates the problem of dirt removal. If we could use nothing but rain water in our laundries, a big part of the problem would cease to exist. For terrestrial water, as it passes through the soil, meets and dissolves considerable quantities of any mineral matter which may be there. Silica, compounds of iron, calcium, magnesium in solution, change the character of water from the "softness" of rain water to what is called "hard" water. Except in a few favored sections of this country, the laundry troubles due to hard water, with the attendant losses in money, efficiency, and durability of clothing, are all too well known.

Hard Water

The regions blessed with a soft water supply are those which are supplied with surface waters, or water which runs over igneous rock from which little soluble mineral matter is obtained, found in areas in the northeastern and the northwestern parts of the United States. Sandy soil built in by the ocean may also give areas of soft water, but wherever the land was formerly the bed of a body of water wherein lime-bearing shells of marine animals accumulated, there limestone abounds in the soil, and the water supply of the region may be excessively hard from the dissolved lime compounds it contains. The Mississippi Basin is such a region. The South-

west suffers in some places from an alkalinity in the soil, which causes the water to be practically unfit for drinking as well as washing purposes.

Difficulty of Softening Hard Water

No one who has experienced the effect of hard water on soap needs an explanation of the statement that the hardness of water is often called its soap-destroying power, nor that the degree of hardness in a given water supply may be measured by the amount of soap it destroys under test conditions. What is meant by soap destruction is that soap is destroyed as a detergent, although it is still a soap. A chemical interchange has taken place between certain compounds held in solution in the water, especially calcium or magnesium sulphates or chlorides, whereby the sodium or potassium component leaves the soap and the calcium or magnesium takes its place, making an insoluble calcium or magnesium soap. This floats in the water as a slimy curd, or settles on the sides of tubs, or too often is trapped in the fibers of the clothing. It has no cleansing action; on the other hand its removal is as necessary, and fully as difficult, as greasy dirt.

These sulphates or chlorides of calcium or magnesium give to the water what is called permanent hardness, in distinction from temporary hardness. Temporary hardness is caused by bicarbonates of calcium and magnesium, held in soluble form by carbon dioxide in the water. Boiling the water drives off carbon dioxide and changes the bicarbonates to carbonates, which are insoluble and settle to the bottom, leaving the water soft so far as these compounds are concerned. Boiling has no similar effect on the sulphates or chlorides, which remain in solution.

Measures of Hardness

Two measures of hardness are employed in estimating the quality of a water supply. The United States Geological Survey has expressed hardness as so many parts of calcium in its calcium carbonate equivalent, in a million parts of water. One part of calcium carbonate in a million parts of water would be called one degree of hardness, and so on. According to their standards, a water of 55 degrees of hardness or under, is soft; from 55 to 100 degrees, moderately soft; from 100 to 200 degrees, moderately hard to hard; from 200 to 500 degrees, hard to excessively hard. By another standard,

one degree of hardness is accepted to mean one grain or .0023 ounce of calcium carbonate in one gallon of water. In round numbers, a United States gallon contains 58,000 grains; therefore one degree of hardness stands for one part of calcium carbonate in 58,000 parts of water. Comparing the two scales, it can be seen that each degree of hardness by the second method of estimation is equivalent to about 17 degrees by the first method, so that a little less than 12 degrees by the second method would coincide with the hardness of 200 degrees according to the United States Geological Survey standard.

What does a hardness of twelve degrees, or really hard water, mean in the actual value of the soap destroyed? At a moderate estimate, every hundred gallons of such water will destroy two pounds of soap, estimating the soap on its dry weight. As bar soaps often contain thirty per cent of water, three pounds at least of soap as purchased will be destroyed, at an approximate loss of thirty cents. This loss, however, is not so significant as losses in time and efficiency, and damage to clothing. These are the real costs, and are hard to measure. The economic problem is apparent.

What can be done with this problem in the home?

Two main phases of the problem have to be considered—costs in soap, time, and labor, and the deterioration of clothing.

Water-softening Methods

Soap and Washing Soda

Let us suppose soap alone is to be used to soften a given amount of hard water. At first the soap unites with the calcium or magnesium ions to form the slimy curd which is calcium or magnesium soap. When all the calcium or magnesium salts are thus used up, a further addition of soap forms suds, showing that it is unchanged soap, ready for cleansing action. And these suds must not be allowed to fall, for the slimy curd must be kept broken up and allowed to float away from the clothing in plentiful suds, else it will settle on the garment. But any substance which can take the place of soap in uniting with the calcium or magnesium compounds *without the formation of a slimy curd*, has a great advantage over soap as a water softener. Several of such substances are in common use, the most common being sodium carbonate in the form of washing soda. Washing soda softens water by forming

insoluble calcium or magnesium carbonate. These carbonates are crystalline salts, and if time is allowed for the action to complete itself, they sink to the bottom of the vessel, leaving the water free from soap-destroying calcium or magnesium ions. This is the general action, whether washing soda, borax, or trisodium phosphate preparations are used. Borax is least efficient of the three, and the most expensive; trisodium phosphate seems to be quite efficient in removing temporary as well as permanent hardness, because of the affinity existing between the calcium or magnesium ions and the phosphate ion, by reason of which insoluble calcium or magnesium phosphate readily forms. All of these compounds are cheaper than soap, and at least six times more efficient, weight for weight. So theoretically this process of water softening seems all that could be desired, but in practice it has its drawbacks.

One problem is the method of determining just the amount of washing soda, for instance, which a given bulk of hard water requires to soften it. If too much is used, its excess will be present as unchanged washing soda, and it may harm certain fabrics or colors. We have to admit that the best we can do is to standardize the process experimentally by finding just the weight or bulk of the softener which will soften a measured bulk of water, so that the first addition of soap produces suds. But water supplies vary from time to time. Moreover, if the water is very hard, the amount of soluble sodium sulphate which is formed in the process may be so great that in itself it will "salt out" or precipitate some of the added soap and prevent its forming suds.

It would be extremely helpful to the housewife if data on her particular problem of hard water could be obtained from the Extension Service of the State College of Agriculture, or from the nearest school of home economics. With this help she might learn how to solve her problem in the most efficient manner.

Other problems are the amounts of time consumed in softening water, and the presence in the water of the precipitated mineral matter. At least fifteen minutes are usually required to complete a softening action with washing soda or similar softeners, and to settle the precipitate, before the soap is added. Then, if the supernatant water can be dipped or poured off, it is in as good condition as possible for first the soap, and then the clothing, to enter.

There are soap products on the market which contain a high percentage of washing soda. No doubt it is present for its water-softening action, quite as much as for any detersive value it may add to the product.

Are there any objections to the general use of such products? The amount of washing soda which they contain may be too much for regions of soft water, and equally too little for very hard water. In such cases there is no time for the washing soda to complete its action before the soap also is drawn into the chemical interchange, with an unnecessary loss of this more expensive ingredient. Moreover, the product of the soap-softening action being a curd, it is more troublesome than the crystalline product either of the soda or phosphate, since more soap must be added to break up and emulsify this curd before the clothes are entered. Therefore, while there are some soap-washing-soda products on the market which are scientifically compounded and efficient in a majority of cases, the choice of these should be governed by the local requirement.

The old method of washing with bar soaps, by which the clothes were put in the tub and then rubbed with the soap, was scientifically wrong. What happened? If the water was hard, it entered the fiber cells—as water will; then came the soap, to form in the cells and the interstices of the fibers the curds of insoluble soap. Naturally the pores of the clothing became choked, and formed a dirt-collecting, non-absorbing menace to body health. A gray appearance often resulted, which required bleaching to remove.

The modern laundry method of softening the water and then producing good suds before the clothes are entered, so that lime soap cannot be precipitated in the fiber, has science and common sense behind it. And if the water is hard, the need of keeping up good suds all the time is imperative.

Zeolite Process

The zeolite process is practical in communities where the hard water problem is serious, and municipal softening should relieve the condition. It can be accomplished by any one of several methods. The zeolite process uses crystalline sodium aluminum silicate, a porous, granular substance having exchange properties. That is, as the water trickles through this substance in the filter, the calcium or magnesium ions are picked up and exchanged for

the sodium ions of the zeolite. So are formed the sodium sulphates, carbonates, bicarbonates, or chlorides, which are not able to destroy soap by replacing its sodium ion, as calcium does. Therefore no insoluble calcium or magnesium soaps can form in water treated by the zeolite process. However, excessively hard water causes an excessive amount of these sodium salts to form, and make trouble, for while sodium carbonate, for instance, cannot destroy soap, it can, as has been said, precipitate it so that it is temporarily useless in forming suds. A considerable amount of soap is needed to make suds, the process being not unlike trying to make a lather in sea water. The alkaline waters of the Southwest contain sodium salts which cause trouble of a similar nature. In some cases acetic acid (in vinegar) or lemon juice must be added to the rinse water to retard the formation of soap grains. Hence the "lemon rinse" after shampooing, in waters of this character.

The installation of a zeolite process on a large scale is limited to large interests, but a smaller household filter of this kind is obtainable. When the zeolite charge is exhausted by the interchange, a solution of common salt is run through to renew it.

Slaked Lime, Calcium Hydroxides and Washing Sodas

Another method, also suited for municipalities or manufacturing plants, uses accurately estimated quantities of slaked lime, calcium hydroxide, and washing soda. This combination removes both temporary and permanent hardness by forming insoluble calcium carbonate and magnesium hydroxide. This process is carried out most efficiently when controlled by a knowledge of the degree of alkalinity of the water, i.e. its pH value at different stages of the softening action. For maximum softening, lime may be added until the pH is about 10.8, after which the washing soda is added. In some cases a combination of this method with the zeolite process has been adopted for the taking care of the sodium salts produced in excessively hard water by the latter method.

Remedy for Iron Contamination

Iron in solution in a water supply causes serious trouble which it is difficult to remedy. As a rule, the iron is found in the form of ferrous bicarbonate. Heat changes the bicarbonate to car-

bonate, a white precipitate which by hydrolysis and oxidation becomes ferric hydroxide. Under the heat of the iron or mangle this deposits as spots of iron-rust. Natural waters containing considerable carbon dioxide are able to dissolve iron to the bicarbonate form; other sources of iron contamination may be the corrosion of water mains or hot water boilers.

The presence of alkali in the wash or rinse waters favors the formation of ferric hydroxide; therefore the detergent process forms rather than removes iron contamination. Bleaching with chlorine bleach or other oxidizing bleaches has no effect on iron-rust spots other than a catalytic action which intensifies the action of the bleach and may cause tendering of the fabric in spots.

The remedy for iron contamination is, first, correction at the source, where this is the water main or boiler. When the rust spot has formed, an acid is required to dissolve and remove it. Acetic acid is too mild to be efficient; oxalic acid, or salts of lemon, or salt and lemon juice—any one of these three is practicable. The excess acid must be neutralized and rinsed out of the fabric.

In commercial laundries a cup of sugar is sometimes put into the wash water before soap is added. The sugar appears to change the nature of the gluey iron hydroxide, which sticks to the clothing, to a granular precipitate which washes away. Borax also has some power to prevent iron hydroxides, if it is put in before soap is added.

Chemical Reactions in Softening Water

The typical reactions which take place when various water softeners are used are here given for those who are interested in the chemistry of the water-softening problem. Where calcium sulphate is used in a reaction, it is understood that a corresponding reaction may take place with magnesium sulphate and the chlorides of both. The reactions with calcium bicarbonate are of course those for the removal of temporary hardness.

When washing soda is used:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

$$Ca(HCO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaHCO_3$$

With modified soda, i.e. a mixture of washing soda and sodium bicarbonate:

$$CaSO_4 + NaHCO_3 = CaCO_3 + NaHSO_4$$

(Modified soda is not as effective as washing soda, about twice as much being required.)

With trisodium phosphate:

$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4$$
$$3Ca(HCO_3)_2 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 6NaHCO_3$$

With borax:

$$CaSO_4 + Na_2B_4O_7 = CaB_4O_7 + Na_2SO_4$$

With calcium hydroxide for temporary hardness:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

With caustic soda:

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + 4NaOH = Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$$
$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

(Caustic soda is not recommended as a water softener because of the effect of excess caustic on clothing, and because only a small amount of carbonate is formed in its reaction with calcium salts. Its greatest efficiency lies in its production of magnesium hydroxide, a very insoluble compound, with magnesium salts, and its efficacy in softening temporary hardness.)

Ammonium hydroxide or household ammonia acts as follows:

$$Ca(HCO_3)_2 + 2NH_4OH = CaCO_3 + (NH_4)_2CO_3 + 2H_2O$$

Then, $(NH_4)_2CO_3 + CaSO_4 = CaCO_3 + (NH_4)_2SO_4$

(But ammonia is not efficient in removing hardness caused by magnesium compounds.)

With the zeolite process:

Sodium aluminum silicate + calcium compounds = calcium aluminum silicate + sodium compounds.

If molecular combining weights are used in the above reaction water of crystallization should be included.

CHAPTER IV

SOAP

Brief History

No cleansing substance has been evolved up to the present time so efficient and practical as soap in all operations where water can be used.

What is soap?

How does it cleanse?

Historically, soap dates back for more than twenty centuries, yet Chevreul threw the light of his researches upon the first question only a little over a hundred years ago. Scientists are still finding answers to the second question.

Conscious chemistry had little to do with the discovery of how to make and use soap. Probably the sacrificial altar was the first soap factory, where the fat of the slain animal dripped through the wood ashes below, and needed only the addition of water to complete a rude transformation into soap. Wood ashes and goat's tallow formed the basic materials for the soap used by the Romans in Pliny's time, but the use of soap as a cleanser was limited then and later to those of high degree. Incidentally it was justly esteemed as a remedy in skin diseases.

Soap seems to have had little to do with household life during the dark ages, but it appears in England as a luxury about the fourteenth or fifteenth century. It is on record that James I, in 1622, granted a monopoly to a company to make three thousand tons of soap for a yearly sum of 20,000 pounds sterling. Users of soap in England were required to pay a tax on the commodity up to 1853.

In this country, soap has been in common use since colonial times. In the years which have elapsed since then the layman's knowledge of the nature of soap has not gone much beyond the fact that fat or grease will combine with lye to form a substance which can remove grease. Perhaps even this fact is not now so universally known as in the days when the lye barrel and the soap kettle were part of the equipment of every household.

The soap manufacturer began to consider soap as a definite chemical compound when Chevreul, in 1815, published his investigations into the nature of fats and oils, and showed that soap is the result of a chemical reaction between the fatty acid groups in fats and the alkali employed in the process. Chemically soap is a salt, and this conception of it, as an ordinary salt with certain solubilities, satisfied chemists for some time. Within recent years, however, advances in the knowledge of colloids and colloidal behavior have thrown new light on the chemical nature of soap, which is now considered to show colloidal properties under certain conditions. It is as a colloid that soap has recently been the subject of extensive study.

Chemistry of Soaps and Their Manufacture

To understand the chemical nature and properties of soap, it is essential to know something of its manufacture.

Raw Materials

The raw materials of soap manufacture are drawn from world-wide sources so far as the fats are concerned; whereas the alkalies are usually limited to sodium or potassium hydroxide, known commonly as caustic soda or caustic potash, or simply as soda or potash lye.

Both the animal and the vegetable kingdom furnish to the soapmaker fats and oils, of such diverse kinds as tallow, lard, bone fat and skin grease, and olive, coconut, corn, palm or palm kernel, peanut, linseed, castor, rapeseed and many other oils.

In recent years the supply of hard fats, most of which are of animal origin and comparatively expensive, has been augmented by a process of hydrogenating certain vegetable oils, such as cottonseed. Thus, when hydrogen is added to these oils, they are changed physically and chemically to products akin to tallow or other solid fats of animals.

The choice of a fat or blend of fats for any given soap is contingent upon a number of considerations. Temperature is one. If the soap is to be used for washing fine fabrics in cool water, tallow soaps are not so suitable as those made from vegetable oils, for the reason that they are not sufficiently soluble at low temperatures and their detergent action is correspondingly lessened. Therefore soaps with a preponderance of hard fats are designed for

general laundry use where the water is expected to be at least 140° F. On the other hand, a soap made entirely from vegetable oils cannot hold nearly as much water as a tallow soap; it is apt to become soft and waste away; it may form a lather freely, but the character of the lather is likely to be less permanent than the close, creamy suds of a soap from harder fats. Olive oil soap is grateful to sensitive skins, but is not a first-grade detergent; soap made from coconut oil alone has sometimes been found to irritate sensitive skins, but is a good detergent in hard water or sea water. The art of the soapmaker includes the blending of fats so that each kind contributes desirable characteristics to a maximum of quality for the class of soap.

So with the choice of the alkali. Sodium and potassium hydroxides form soaps which are soluble in water and have other properties which aid in detergency. Sodium soaps hold less water than do potassium soaps of the same fats or oils, therefore they are hard soaps even when vegetable oils are used, whereas potassium soaps made from the same oil stocks usually are soft soaps. Since in the average cleansing operation a hard soap is more convenient than a soft soap, sodium hydroxide is the common alkali in soapmaking, potassium hydroxide being used for special products such as some liquid soaps and shampooing preparations.

There are soaps which cannot be classed as detergents, since they are not soluble in water. They are made with the hydroxides of such metals as zinc and lead. Zinc stearate is a soap used for skin affections, and the lead soaps of linseed and other oils are found in paints.

What is the interaction of these fats or oils, and the alkali?

The forty- or fifty-pound capacity of the colonial soap kettle has been increased to the million-pound capacity of the modern soap kettle, rule-of-thumb processes have become laboratory-controlled ones, but the essential reactions involved in the making of a soap have not altered with the years.

Chemical Reactions

Whatever their source, fats and oils have a common nature. They are typically glycerides, or esters formed by the interaction of the alcohol glycerol, and fatty acids. Other products may be associated with fats in natural sources, products which have

likenesses to fats with slightly different chemical compositions, but these are in minor amounts. In this union of glycerol and fatty acids to make a fat, water is split out, so that the reaction for the formation of a typical fat, and its formula, may be:

$$3\ C_{17}H_{35}COOH + C_3H_5(OH)_3 = (C_{17}H_{35}COO)_3C_3H_5 + 3\ H_2O.$$

Fatty acid plus glycerol equals fat plus water. A fat, then, is potentially fatty acids and glycerol, because it can split into these products when the three molecules of water which were produced in the synthesis of a fat, go back into it on hydrolysis.

This hydrolysis or fat-splitting is called saponification, particularly when an alkali produces hydrolysis, as in soapmaking.

In the hydrolysis of organic salts or esters, such as fats, a catalyzer is usually necessary, and causes the action to take place without itself being directly concerned therein. Catalyzers may be high heat alone, which in the case of a fat would be destructive for soapmaking purposes, or less heat together with a dilute acid or alkali. Both acid and alkali are employed in different methods of soapmaking, but the use of alkali, being the common method, will be considered first.

Thinking of the catalytic action of the alkali, as a carrier of water to the molecule of fat, we can express the result of this hydrolysis as follows:

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O = 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

The free fatty acids now find and unite with the alkali present to form soap, leaving the glycerol as a by-product:

$$C_{17}H_{35}COOH + NaOH = C_{17}H_{35}COONa + H_2O.$$

It is customary to condense these two reactions into one, in which catalysis is understood, and the chemical effect of the alkali is emphasized:

$$(C_{17}H_{35}COO)_3C_3H_5 + 3NaOH = 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

Soap manufacturers achieve the above result by any one of several processes: the cold process, the hot process, the Twitchell process, etc. Chief of these is the hot process, by which soaps are made at the boiling temperature.

Manufacturing Methods

Boiled soaps

If the solid fats are to predominate in a soap, the hot process is almost essential, because such fats do not emulsify easily at

low temperatures, and the production of an emulsion is the first aim in soapmaking. An emulsion in this case is a minute subdivision of liquid fat particles in the solution of caustic alkali, the alkali acting temporarily as an emulsifying agent. It is through this subdivision, of microscopic fineness of particles with an enormous surface area, that the surrounding alkali can reach each particle of the mass of fat, and begin its chemical action. Furthermore, the temperature employed in the hot process accelerates chemical action and thus produces soap much more rapidly than by the cold process. As soap forms, it stabilizes the emulsion already made and aids in emulsifying other particles of fat, so taking an active part in the completion of the process.

In the large soap kettle, therefore, a mixture of fats in a melted condition is entered, and boiled with open steam for a time and then with rather dilute sodium hydroxide until the mass passes through the emulsion stage and the required degree of saponification is reached. This process is called the *stock change*. It is an interesting fact that the concentration of the alkali must be carefully adjusted to the nature of the fats used. If these contain a large percentage of the higher fatty acids, the soaps which form are readily "salted out" or curdled by the immediate addition of a strong concentration of alkaline solution, whereas soaps made from fats rich in the lower fatty acids, such as coconut oil and castor oil soaps, are not easily salted out by any concentration of alkali, weak or strong.

So, in making household soap, if the fats collected for soapmaking are principally of the tallow type, a solution of lye of high concentration cannot be used, or the same difficulty will arise, and the soap will grain or curdle, even though the actual amount of lye may be in correct ratio to the amount of fat. The difficulty can be remedied by adding water and so reducing the concentration. On the other hand, household soaps made from semisolid fats or from oils will not curdle with a fairly concentrated lye; in fact, they require it to solidify.

When the right degree of saponification is reached in the stock change above described, the soap is salted out or grained in the same kettle, in order that as it floats on the top in grains it may separate from the spent lye and glycerol and from impurities. The salting out is accomplished by a strong solution of either common salt or caustic alkali. A saturated salt solution is

usually used, although strong alkali is more effective in salting out soaps made from lower fatty acids such as are in coconut oil.

An application of this salting-out phenomenon may be carried over to the evaluation of soaps for household use. A soap made mostly from hard fats will curdle or grain more readily in water containing common salt or the salts dissolved in hard water, than will one incorporating considerable coconut or other vegetable oils. This is one reason why soaps made at home from a tallow base often give unsatisfactory suds. Soap made principally from coconut oil is particularly useful on shipboard or elsewhere where salt water is used.

After the graining process is completed, the contents of the kettle are allowed to stand to facilitate a separation into two layers, the upper one of grained or curd soap, the lower of spent lye, glycerol, and brine. This latter mixture is drawn off and treated for the recovery of glycerol. The soap mass may then be boiled with water or open steam until the grains disappear and the soap has a "closed" appearance.

Gradual addition of strong caustic soda to the soap, and boiling, now effect what is known as the *strength change*, in which complete saponification of hitherto unsaponified fats takes place. The soap is again grained by the strong lye, and on standing, the excess lye, called half-spent lye, is drawn off from the bottom of the kettle.

Again the soap grains are closed by adding water and boiling until the right degree of closeness is reached. When the mixture stands for some time, the purer soap forms at the top, and a layer of inferior grade, called nigre, lies below. This is the process of *settling*.

The good soap produced at this stage consists of about sixty-two to sixty-four per cent combined fatty acids, and about thirty per cent water. It is pumped out of the kettle while still in the fluid state, to be cooled at once for cutting into bars, or more commonly, to have additions made to it in the crutcher. The nigre may be incorporated in other soaps of inferior quality.

Cold Process Soaps

The cold process of soap manufacture is adapted to fats which are fluid at ordinary temperatures, and allow an emulsion to form and chemical action to follow without high heat. The coconut

oil type of fat is particularly suitable. The fat is warmed to about 80° F. and the requisite amount of strong alkaline solution is added. After thorough mixing, the kettle is covered and allowed to stand. More time is required for complete saponification to take place than when heat is used to accelerate chemical action.

This is the easiest and cheapest method of making soap, the one employed for some toilet and transparent soaps, and almost entirely for soaps made in the household. It has its disadvantages. Fats and oils cannot be saponified completely, as a rule, without an excess of alkali, and in this process an excess cannot be added if a balanced soap is to be produced. Even so, the balanced soap may not follow, so that there is a possibility of having both free fat and uncombined alkali present. Free fat tends to become rancid, and free alkali in a toilet soap has an irritating effect on the skin. The most happy results with this process come from using coconut oil, which is capable of ready saponification with strong lye. The addition of castor oil produces a transparent soap, the transparency further enhanced by additions of sugar in cheap varieties.

When soaps are made at home by the cold process, as they usually are, the fats should not be entirely of the tallow type, but a blend of hard and soft kinds. They should be as free from impurities as possible, for by this method no impurities can be separated from the soap. The proportion of alkali to fat must be determined by weight and rule, and the strong solution of the former slowly stirred into the slightly warmed fat until a thorough blend is made. The product should then be covered and allowed to stand for saponification to complete itself. At least three weeks are needed for the soap to come to the right condition of dryness and texture, although it may be cut into bars as soon as it is firm enough to handle.

The Twitchell Process

By the Twitchell process the fat or oil is hydrolyzed by an acid catalyst, the fatty acids separated and made to unite with the chemically computed amount of alkali. The latter may be either caustic or carbonated alkali, sodium carbonate being frequently used. The process is expensive, but it yields accurately controlled products.

Soft Soaps

Potassium hydroxide is the usual alkali employed for soft soaps, although some sodium hydroxide may be incorporated. The fatty material is almost always an oil, often linseed oil. If some harder fat is present, "figging" is apt to occur, a process which is a crystallization of particles of soap from these harder stocks. Made from oils alone, a soft soap remains clear and translucent.

There is only one operation in making a soft soap, a single boiling with dilute alkali and later with stronger alkali, until saponification is complete. The product contains the glycerol and any impurities.

Commercial Types

The consumer has a certain background for choice if she understands the market types of soaps, the average composition and characteristics of each type, and the particular purposes for which each is fitted. They will be mentioned briefly here, and in more detail as to composition in Chapter X.

Bar Soaps

Two types of laundry soap in bars are commonly found—white and yellow. White laundry soaps contain sodium silicate, popularly known as water glass. An excessive amount of silicate, as much as forty per cent, is sometimes incorporated in poorly made white laundry soaps. A discussion of the value of sodium silicate and other additions to soap is given in the next chapter, which should be read in connection with this section.

Hard water soaps in bars, for toilet or semi-toilet use, are usually silicated soaps.

Yellow laundry soap may contain some sodium silicate, but the chief addition is rosin soap, blended with the soap made from fats. Rosin soaps are yellow to brown, so the color of the finished product is always yellow if any appreciable amount of rosin soap is incorporated. It is correct to speak of rosin soap rather than rosin as an addition to this type of soap, since rosin, which contains acids, is made into a soap with caustic alkali before blending with the ordinary soap made from fats. A typical yellow laundry soap may contain about thirty per cent moisture, and about the same amount of rosin soap, the balance being principally soap

made from mixed fats. In both yellow and white laundry soaps small amounts of free alkali, sodium chloride, and carbonated soda are usually found. The free alkali should not exceed 0.5 per cent.

Mottled bar soaps may owe their appearance to several causes. They may be made from low-grade fats and strong lye, in such a way that impurities do not settle out, but stay in the soap and give it a marbled appearance. Sometimes this effect is heightened by the addition of copperas or copper sulphate or of ultramarine to make a blue mottled soap. Such soaps cannot be considered high-grade products, and are quite apt to contain free alkali in excess, as well as salt, sodium silicate and usually sodium carbonate.

Floating bar soaps are made by forcing air through the soap while it is hot, or at about 170° F. As a rule floating soaps are of the semi-toilet or bath type, and of good quality. These soaps usually lather well because of a fat-oil blend as the base.

Flake Soaps

As a rule, flake soaps are designed for the washing of fine fabrics, and include some well known and long established products. The fats which predominate in these products designed for washing delicate fabrics are of the oil variety, such as coconut, peanut, olive and cottonseed oils, in order that the soaps may be efficient detergents in the cool water used.

Soap Chips

Soap chips are designed for quick solution in the laundry tub, and are especially adapted to newer methods of laundering and the use of machines. Soap chips are seldom as pure and mild as the flake soaps mentioned above. A few products are found which are mild and safe for wools, silks, and synthetic fibers, but on the whole it is better to choose these products for the general laundry work rather than the hand basin type of laundering. Soap chips are more economical to purchase than bar soaps from the standpoint of moisture content, as they seldom contain more than half the amount of water found in bars, and often their moisture runs as low as five to ten per cent.

Powdered Soaps

Powdered soaps have recently become popular. As a rule, the finer the subdivision of a soap, the more rapid its solution. The

time-saving aim partly accounts for the increased popularity of forms of soaps such as these. A powdered soap may have large additions of other powdered substances made to it; for instance, it may contain so much washing soda as to be essentially a soap powder, which is a product understood to be chiefly washing soda. The consumer should be wary about the indiscriminate purchase of these products unless they can boast of a well established reputation for value. Many such soaps are low in detergent value compared with the price charged.

Grains and Beads

Soaps in grains and beads have in common with powdered soaps the property of quick solution, without requiring hot water to effect this. The bead form is the quickest to go into solution, as it is more or less hollow, while the grain is solid. Bead soaps are made by spraying melted soap from high towers down through a current of heated air. These soaps are often of good quality, containing in some cases moderate amounts of carbonated soda and sodium silicate when advertised for the general laundry, and when designed for fine fabrics being equivalent to the fine flaked soaps.

Soap Powders

Soap powders designed for softening hard water and aiding in the coarser kinds of cleansing are, as has been said, essentially carbonated soda compounds mixed with more or less soap. The minimum amount of the latter is generally considered to be about fifteen per cent. Recently other ingredients have been found, particularly sodium silicate and trisodium phosphate.

Trisodium Phosphate Powders

Trisodium phosphate powders are new forms of detergents, and represent possibilities which have not yet been fully tried out. Very few contain any soap, and this is one of the advertising points made by many of these preparations, the plea being that soapsuds are difficult to remove from bottles, glassware, etc. Trisodium phosphate is an excellent water softener, has considerable antiseptic value, and as a mild alkali has a detergent action; yet as a detergent it depends chiefly upon chemical action for its effect, and as an alkali, the force of the alkali is released rapidly

in the detergent solution. With soap, the release of the alkali is gradual, and the cleansing action, being mostly physical, has less destructive effect on the fiber structure. The very fact that these preparations make no suds is a handicap in cleansing, because there is nothing to hold up and float off particles of dirt after they are dislodged, and they are likely to settle back in the clothing. It is in this type of product that the greatest variety of new forms is appearing, and here the consumer should try to evaluate a purchase with some care before using it for all the purposes for which it may recommend itself. Nevertheless, the advantage of these products for the uses mentioned above cannot be gainsaid.

Liquid Soaps and Soap Jellies

Liquid soaps and jellies are without doubt the least economical of all forms of soaps, and perhaps show as wide a range of quality as any type. The output of these in small packages for household use as specialties has been steadily increasing, varying from bottled products for washing silks and wools made of a potash base combined with a good oil stock and mild in reaction, to tin cans of liquids and jellies recommended for every variety of cleansing. The greatest criticism of this type of product as a whole is its cost compared with the actual detergent material it contains.

CHAPTER V

SOAP ADDITIONS

Builders

Very few laundry soaps are soap and nothing more. Additions are made which may serve a useful purpose, or which may be adulterants. When these additions, usually some form of alkali, build up a soap so that it is supposed to perform its work better under given circumstances than the soap could do, they are called "builders."

As builders, free alkali may be useful in neutralizing free fatty acids in greasy dirt; washing soda may aid in softening water not softened by previous treatment; rosin soap may increase the sudsing action of a soap in cool water; sodium silicate adds to the colloidal activity of a soap. All these are builders in common use, yet the presence of one or more of them in a soap may not always be desirable. The consumer should know in what ways they may limit or extend the uses to which the soap can be put, and as far as possible should be able to recognize their presence.

Rosin

Rosin is a by-product of the turpentine industry, the turpentine being obtained from the sap of the long-leaf yellow pine growing in the South Atlantic and Gulf States. The chief constituent of rosin is abietic acid, $C_{19}H_{29}COOH$, which combines with caustic soda in soapmaking to form the sodium salt, $C_{19}H_{29}COONa$, or rosin soap. Rosin soap was one of the earliest additions to be made to a fat soap, and as its cost has been uniformly below that of the fat used for the particular grade of soap, the typical yellow laundry soap has been able to sell at a price lower than the price at which it would have sold had it been made from fats alone.

However, the fact that rosin soap cheapens a soap is not equivalent to saying that it is an adulterant, and without value. Those who do not wish a rosin soap need not purchase one, for the well known yellow color and the odor which rosin soap in any quantity

imparts to the product mark these soaps very clearly. The common practice has been to incorporate into a bar laundry soap of this kind about twenty to thirty per cent of rosin soap, or about the equivalent of the amount of fat soap present. Soapmakers justify the use of rosin for the following reasons:

Rosin soap, they say, is more soluble in cool water than soaps made from the tallow fats; therefore the sudsing and detergent power of such a soap is increased. As rosin soap is a colloid, an important point is scored, for it will have a colloid's cleansing action, similar to that of the fat soaps. Rosin soap has an inhibiting action on rancidity.

An objection which is sometimes made to these products is that rosin acid soap may result from hydrolysis, or insoluble rosin soap may form in hard water, both of which when deposited on the clothing may leave yellow streaks or stains. But this should not ordinarily happen if a moderate amount of rosin soap is incorporated and if good suds are kept up. There seems to be no reason why a well made rosin-fat-soap should not be a satisfactory product for the rougher kinds of cleansing and general laundry work.

Free Caustic Alkali

The presence of free or immediately available alkali is one objective in allowing an excess of alkali to be present in some soaps. In certain cleansing operations additional strength in the soap may be needed to remove greasy soil and stains, for instance, in washing the working clothes of laborers. Free caustic in a soap also retards the hydrolysis of the soap and so acts as a stimulus to its activity as a colloid and an emulsifier. But caustic alkali in excess has a destructive action on soap itself, is fraught with danger to fabrics, even to cotton, at high temperatures, and its presence should be kept within certain bounds even in products designed for rough laundry work. The specification of the United States Government for ordinary laundry soap requires that the amount of free alkali calculated as sodium hydroxide shall not exceed 0.5 per cent. The effect of sodium hydroxide on the textile fibers has been mentioned in a previous chapter, but it may be emphasized that the danger in using soaps containing free alkali is cumulative, since the caustic alkali is absorbed into the body of the fiber, from whence it is difficult to rinse it completely. Under

the heat of the iron it concentrates its strength and increases its chemical action on the fabric.

The consumer has no very definite way of recognizing a soap strong with free alkali except that it may roughen and dry her hands. With different skin susceptibilities, what may seem a strong soap to one may not to another. If the consumer will procure some red litmus paper, and lay a dampened piece on the freshly cut, dry surface of the soap sample, the intensity of the change to blue will give some indication of the degree of alkalinity, especially if the test is made at the same time on several types of soaps in comparison.

Carbonated Soda

Very few soaps for general laundry purposes are entirely free from some form of carbonated soda, either anhydrous sodium carbonate or hydrated sal soda called washing soda. Modified soda is sometimes used, being slightly less alkaline in its reaction. It is sometimes called sodium sesquicarbonate, and is a mixture of sodium carbonate and bicarbonate. The bicarbonate checks the hydrolysis and alkalinity of the carbonate, but this modifying action is temporary in the presence of heat, which converts the bicarbonate to carbonate. Modified soda is not for this reason particularly advantageous over sal soda, and it has the disadvantage common to the caustic and carbonated alkalies of penetrating the fiber and being a slow rinser. The use of carbonated soda in soap for water-softening purposes is not especially desirable, for, as has been pointed out, water softening should precede the entrance of soap. What, then, is the chief function of this builder in soap?

Where a soap is desired which shall have a detergent action due to free alkali, and therefore will cleanse by "cutting" grease, combining with free fatty acids and acid dirt, and supplement the physical action of a neutral soap in removing dirt, soda ash, sal soda, or modified soda meets the requirement and presents this alkali in a form less destructive to fabrics than that of a caustic alkali. The reason is that only ten to twenty per cent (in round numbers) of its alkali or hydroxyl ions are released at any one time in hydrolysis, whereas the alkali of a solution of sodium hydroxide is felt at once in almost one hundred per cent strength. Moreover, these salts, being salts of a strong base and a weak

acid, have a certain amount of "buffer" action, and prevent the rapid concentration of hydroxyl ions due to the hydrolysis of the soap. So far, so good. But a considerable amount of carbonated soda gives to a soap a total amount of alkali which is destructive in differing degrees to all fibers, especially at elevated temperatures. Those soaps which are called rinsing soaps, and which depend upon a large amount of carbonated soda or other alkaline salts for their power to rinse the clothes clean without much mechanical action, achieve this effect largely through the chemical action of the soap product on the fabric, at the risk of deteriorating the fibers of delicate or susceptible fabrics.

The addition of a small amount of carbonated soda to a soap has some effect in lowering surface tension and increasing sudsing power, but a low surface tension is not a sole measure of cleansing power. The surface tension of a soap solution is progressively lowered as more soap is added to it, but there comes a point of concentration beyond which the further addition of soap retards rather than promotes cleansing action. Therefore, unless the presence of washing soda in a soap solution is promoting cleanliness in some other way, its action in lowering surface tension may not be significant.

The presence of a carbonate may be detected by adding a little vinegar to the finely-divided soap product. The vinegar causes effervescence and evolution of carbon dioxide if a carbonate is present. A mild amount of effervescence may be expected in a soap for general use.

Sodium Silicate

This substance forms solutions with colloidal properties, and therefore comes nearer to soap in its physical cleansing action than any other builder with the possible exception of rosin soap. That is, as explained in the following chapter, it has a part in the emulsifying, suspending, and adsorptive action of soap toward dirt. It also restrains the dissociation of soap in water, and is a water softener.

Sodium silicate itself is a mild alkali, relatively speaking, the degree of alkalinity depending on the composition of the particular brand. The mildest commercial brand has a pH of about 9.4, which is less than the alkalinity of most mild soaps in solution. Brands which have an increased amount of sodium oxide in pro-

portion to the silica are higher in alkalinity; those containing proportionately more silica are less alkaline and are the ones usually employed as soap builders. The silicates used by the soapmaker may be represented by the formula $Na_2O(SiO_2)_x$, in which x has a value of 2 to 3.3.

Silicates harden on drying; therefore from their use results a hard soap which does not waste away even though the fatty base is entirely of oils. This effects a saving. They are cheaper than fats, although more expensive than carbonated soda, and this makes it possible to market white laundry soap in bar form at a price competitive with yellow laundry soap containing rosin soap. The question of the amount of silicate is the important one. Although silicates have detergent value, they do not equal soap in this respect, and if for the sake of cheapening the product the silicate content is run up to thirty or even forty per cent, the result is an inferior and adulterated article. The name of a reputable soap manufacturer is the best guarantee against such adulteration.

A silicated soap does not become rancid so readily as one made from the soft fats, so that, together with its property of keeping hard, its quality does not deteriorate with use. If well made, silicated soap may be a very good soap for the general laundry, but it is not the best choice for silk, wool, and synthetic fibers.

The consumer does not need a household test for a silicated soap, for all white bar soaps for laundry use are such. Soap chips may also contain silicate of soda, but rarely in excessive amounts.

Naphtha

If by the term "naphtha" is meant those hydrocarbon oils of the density of gasoline and cleaning naphtha, then naphtha soaps have not always contained naphtha, but a rather heavier grade of petroleum distillate. The lighter naphtha is apt to volatilize from the soap to such an extent that by the time it reaches the consumer little is left but the name.

It is claimed for naphtha, or similar hydrocarbons in a soap, that it increases the solvent action on grease, lowers the interfacial tension between a solution of soap and any oil with which it may come in contact, and aids in emulsification of greasy dirt. It may be incorporated to the extent of ten per cent of the soap mass, and if it reaches the consumer with that approximate com-

position, there is no doubt of its efficacy as a detergent. Lowering that percentage toward the vanishing point raises the question of how efficacious the amount of naphtha which is present may be when distributed through a tub full of water.

White naphtha soaps are also silicated, and are designed for general laundry work. If naphtha is incorporated in a soap, the label states the fact.

Bleaches

The usual bleach incorporated in a soap, in the few cases on the market where a soap carries a bleach, is either sodium peroxide or sodium perborate. The former is distinctly harmful to fabrics; the latter is mild by comparison. Sodium peroxide in solution hydrolyzes to caustic soda and hydrogen peroxide, which in turn breaks up into water and free or atomic oxygen. This oxygen constitutes the bleach, since it attacks and destroys coloring matter or discolorations in the fiber. Sodium perborate also releases oxygen in a way similar to the peroxide, but with less causticity.

All bleaching, whether by the sun or by chemicals, is attended by some chemical action on the fiber. It is well known that when linen is full-bleached it is from twenty to twenty-five per cent weaker than it is in the unbleached state. Curtains, whether of silk, cotton, or linen, hung in a sunny window, become tender in time through the action of air and sunlight. Cotton degenerates from cellulose to an oxycellulose, or a cellulose in partly hydrolyzed form, when overbleached, and oxycellulose is a step toward decomposition. Cellulose may become an oxycellulose through the action of the ozone of the air, or of oxygen in a form similar to ozone when released from the following: hydrogen or sodium peroxide, sodium perborate, potassium permanganate; or the action of caustic soda at high temperatures in the presence of air.

One of the criticisms to be made of the treatment of clothing in some commercial laundries, especially small laundries operated independently and often unintelligently, is the practice of overbleaching or uncontrolled bleaching. It is quite common for white goods to be returned harsh from precipitated calcium salts deposited in the bleaching process, and brittle from the formation of oxycellulose.

In the home, bleaching should not be overdone, nor habitually

done. Thorough cleansing with a good soap should obviate the need, especially if body and bed linen are not allowed to become unduly soiled. Clean linen need not be dead white and weakened. Some of the bleaching soaps are excellent for occasional use, since the amount of bleach is less and the action more controlled than when an unmixed bleach such as Javelle water or a similar bottled preparation is used. The latter should be kept for special needs and used at low temperatures and in weak dilution.

Bleaching soaps, by liberating oxygen, also act under controlled conditions as disinfectants. All soaps have some antiseptic properties, but an oxygen-releasing soap carries these to a greater degree than the ordinary product. As these soaps are usually in powder or grain form, they are likely to suffer a loss of oxygen if left open to the air or allowed to get damp. This is one case where it is more economical to purchase a small package of the product than a large one, as far as the keeping quality is concerned.

Before washing colored goods with bleaching soap an experiment should be conducted to ascertain the effect of the soap on colored material.

If a soap product purports to contain an oxygen bleach, a simple test should prove it. A strong solution of the soap, allowed to stand quietly in a tumbler until a jelly forms, will have this jelly perforated with bubbles of gas provided oxygen is being given off.

Borax

Borax, a mildly alkaline salt, is found in a number of detergents on the market, and in most cases the package states its presence. Its mild alkalinity makes it a safe constituent at cool temperatures in a solution for the washing of wool and silk; on the other hand, its low detergent value gives no definitely increased value to an otherwise good soap. As a crystalline substance it does not have the physical action of a colloid in cleansing; it has only slight water-softening action and an equally slight bleaching effect; it has some effect in preventing the precipitation of iron-rust on a fabric, and some suds-sustaining power. Altogether, if the product is well made, its borax content does not make it very much better. Its advantage in soap manufacturing lies in the fact that it stiffens the soap mixture, a property shared by all the sodium salts used as builders.

Trisodium Phosphate

Trisodium phosphate, a crystalline substance, has lately come into prominence as an addition to soap in powdered form, or as a detergent unmixed with soap. It compares with borax as to alkalinity, and has about one-fourth the available alkali of soda ash. In the *Manual of Standard Practice for Power Laundry Washroom*, published by the Laundryowners' National Association, the following comparison of the alkaline values of the several builders most frequently used is given:

One pound of soda ash is equivalent to:
1.1 pounds sodium carbonate monohydrate
2.5 pounds neutral or modified soda
2.7 pounds sal soda
4 pounds trisodium phosphate, crystalline
5 pounds borax

Trisodium phosphate brings to the detergency problem some superiority as a water softener, and the chemical action of a mild alkali. Used alone as a detergent, however, it has little more efficacy than a solution of borax would have, that is, it may cleanse to a degree, but the absence of suds causes the loosened dirt to fall back on the clothing instead of being floated off. Where the absence of suds is desirable, as in cleaning dairy equipment, bottles, window glass, etc., these products are admirable, and as water softeners, to be used before the soap enters the tub, they give satisfaction. But they are not the equal of a mild soap in laundering fine fabrics, in spite of advertising which claims superiority for this purpose.

As a rule, trisodium phosphate preparations have appeared on the market unmixed with soap, or practically so, in packages with appealing names. If such a product makes no suds when dissolved in water, the consumer may be certain it is principally trisodium phosphate.

Fillers

The United States Bureau of Standards distinguishes between alkaline salts, which it calls "builders," in soaps, and other substances which it designates as "fillers." Yet anything which serves a useful purpose in a soap might in a broad sense be called a builder. For instance, cane sugar is often used in transparent

soaps to give the condition of transparency, and is not strictly a filler. But excess sodium chloride, and clay, chalk, or other earthy materials which add weight without serving a useful purpose are certainly fillers and adulterants. Filled soaps were more common in former years than now. A cheap family soap might contain more rosin soap than fat soap, and in addition soda ash and silicate as builders, and talcum, silex or marble flour as fillers. Soaps which have earthy material added for abrasive purposes are not in this class of filled soaps.

CHAPTER VI

CLEANSING ACTION OF SOAP

Soap as a Colloidal Solution in Water

As long as the field of colloid chemistry is not completely explored, and as long as the colloid state is not easily defined, the whole story of how soap cleanses may not be told; for the fact that soap is considered to behave as a colloid when in ordinary solution has opened up increasing research, out of which has come most of the explanations of its detergent action.

Soap may be found in many physical states. It may be in colloidal solution in water, that is, in what is called the sol or hydrosol state. It may be in true solution in alcohol, and also in water at high temperature; it may have set to a clear jelly called a "gel," in which the solvent, water, is dissolved in the soap and held in a network of the latter; it may be in a crystalline or a curd state. But of all these forms, that in which the soap is in colloidal solution, has been found the most effective in cleansing.

In a study of soaps which aims to have a practical as well as an inclusive educational value, there is little need to give much space to the properties of colloids in general. But it may clear the way to an understanding of the behavior of soap as a cleanser to note some of the characteristics of a colloidal solution such as soap may form in water.

A colloidal solution is quite different from a true solution of soap. In a true solution the soap is dispersed through the water as single molecules beyond the range of visibility of a powerful microscope, and a single-phase system results. Such a solution looks water clear. But in a colloidal solution there exists a two-phase system, namely, water and soap, in which the particles of soap, while still invisible to the eye, are larger than molecules. Such a solution has an opalescent appearance. With the aid of an ultra-microscope, by which a powerful beam of light is focused on a solution, the colloidal particles within the solution appear under high magnification as bright points of diffracted light, much

as a narrow beam of light entering a darkened room shows the presence of dust motes.

Physical Properties of Colloidal Particles

The physical properties of these colloidal particles of soap existing in a sol are of the greatest significance in explaining the cleansing action of soap.

Brownian Movement

For example, with the ultra-microscope, a constant zigzag movement of these particles is seen, a movement evidently resulting from a bombardment by the molecules of water. These constantly moving soap bodies in their turn bombard aggregates of dirt, begin to peptize or disintegrate them, and keep them in motion until, by the further action of the soap together with mechanical agitation, they are floated away from the garment. This constant movement in a sol is called the Brownian movement, from the botanist Brown, who was the first to observe it. Without this ceaseless motion it is doubtful whether the soap particles could resist the force of gravity which tends to pull them down to an agglomeration at the bottom of the vessel.

Great Surface Area for Action

Since the mass of soap exists in water in an infinite number of dispersed particles, an enormous surface area is presented by the totality of these particles as an arena for physical action between soap and dirt. Analogous to this increase in area is the breaking up of a mass of fat, when it is emulsified, into minute droplets, thereby increasing tremendously the field of chemical action between enzyme and fat in digestion. This property of forming a type of solution in which an enormous surface is exposed in proportion to the bulk of the substance is a characteristic of colloids.

Adsorption

This great surface area has a further significance. Certain substances show a tendency to adhere to other substances, a phenomenon which is noticed when water, for example, wets a glass surface. Adhesion is possible if the force exerted between molecules of different masses is greater than an opposite force, perhaps valence, which causes a cohesion between molecules of the

same mass. The water molecules adhere to the glass, and it is equally true that the glass molecules adhere to the water. In the highly subdivided phase of the soap mass in a sol, the extended surface area increases the opportunity for these adherences. Very close adherences, especially where no water or air film intervenes, come under the phenomena of *adsorption* in its different phases. For instance, charcoal adsorbs gases into its pores; a solid may adsorb a liquid so that air is displaced and the solid is wet by the liquid; two powders of different degrees of fineness may be mixed, and the coarser may have each of its particles entirely coated by the finer. These are classed as adsorption phenomena, and all colloids may show adsorptive power. If a visual presentation of the particles of soap in colloidal solution could be made, with dirt present in the solution, no doubt a concentration of adsorbed bodies at the boundary layers might be seen. Dirt will exhaust soap from a washing solution because of this mutual tendency to adhere.

The adsorptive power of surfaces is proportional to the area, but adsorption is selective, and the degree of adsorption varies with the adsorbent. For instance, in the well known experiment of covering the surface of a cone of filter paper with lampblack, and passing water through, a slight amount of the lampblack is carried through with the water in the first filtration, but in a second filtering the water comes through clear. The pores of the filter paper have now adsorbed sufficient of the lampblack particles to close them against further passage; it is evident that water and lampblack have little mutual adsorbent power, in that water is not able to pull these particles away from and through the filter paper. Now if a soap solution is passed through, a considerable amount of lampblack passes at once through the filter paper with the soap, and on repeated filtrations more and more is removed until the paper is clean. Evidently adsorption is selective here, the lampblack and soap particles having a greater pull each for the other than the former to the fibers of the filter paper. We may liken the cellulose of the filter paper to our clothing, the dirt which is adsorbed by clothing being affected by a soap solution as the lampblack is on the filter paper.

No doubt the greater efficacy of the soap solution over the water in this case is due in part to the low surface tension of a soap solution and its consequent power to spread evenly over a surface

and wet it. Low surface tension and adsorption interact in this case. Many authorities attribute the cleansing action of soap chiefly to the very low surface tension of its solution.

Low Surface Tension

Here again it is difficult to make clear what the term "low surface tension" means in the case of a soap solution without some explanation of the physics of surface tension.

To derive a concept of surface tension we must visualize the condition of the molecules lying in the surface film of a fluid. The molecules below the surface are acted upon equally on all sides by the attraction of neighboring molecules, so that they are in a state of zero pressure or pull as a resultant of these opposing forces; the molecules lying in the surface layer, however, have no pull upon them from above, and therefore they remain in the surface only by their power to resist the pull from the sides and below. The amount of force by which they resist this combined pull is their surface energy, and the measure of this resistance constitutes their surface tension. For example, the molecules in the surface film of pure water under standard conditions of temperature and pressure are pulled by, or resist, a force equivalent to about 72 dynes; therefore we say that the standard surface tension of pure water is 72 dynes, on a strip of the surface one centimeter wide. (A pull of one gram is equal to 980 dynes.)

When soap is added to water, the concentration in the surface film is greater than in the mass of the solution, consequently the pull from below is less proportionately, and surface tension is lowered. A soap solution has about the lowest surface tension of any known solution, being on an average a little more than one-third that of pure water.

Some results of this difference in the surface tension of water and of soap solutions are seen in the behavior of the two fluids.

Since the pull on a molecule lying on the surface is inward, and equal on each molecule in the surface film, then a drop of liquid will tend to be drawn into a spherical form. That is, as the surface molecules feel the pull they are drawn into the smallest possible area, which is the sphere. This process is shown by raindrops in the air, or soap bubbles. When the water lies on a greasy plate, where the adhesion affinity of water and grease is

less than the cohesive force existing between the water molecules, the spherical shape of the drop is not interfered with. But a soap solution with its low surface tension is not drawn up so far from the surface, even a greasy one, and the drop flattens out and wets the surface of the grease. Consequently with this spreading power a soap solution can penetrate the fibers of the clothing to a far greater degree than can clear water, and it is equally true that its surface can be penetrated more easily by dirt than the surface of clear water.

The surface of the clothing is more easily wetted also; therefore the soap penetrates the fiber mass under the dirt and tends to loosen the latter.

As water approaches the critical temperature at which it becomes a gas its surface tension diminishes. So with soap solutions; the higher the temperature, the lower the surface tension. Surface tension also decreases with increased concentration of soap in water. But we are not justified in saying that low surface tension is an exact measure of detergent power; that the lower the tension of the solution the greater its detergent action. Low surface tension is a fundamental necessity in cleansing, but if it is the result of too high a concentration of soap the solution will not cleanse well. Beyond a certain optimum strength it loses emulsifying value, and when emulsifying power drops, dirt drops out and settles back on the clothing. By experimentation it has been found that a solution of soap of about 0.25 per cent strength is a good average for efficient work. Neither is a low surface tension resulting from high temperature desirable in all cases, a point discussed in the chapter on temperature.

The differences in surface tension between soaps of different types are slight enough to be almost negligible, but the difference between a soap and a cleanser of another kind, such as trisodium phosphate or sodium carbonate, is great. These cleansers give surface tension readings only three or four dynes lower than distilled water. Such alkaline salts, taken alone, cannot stretch over a surface and wet it as readily as soap solutions do.

Interfacial Tension

Solutions having a low surface tension will also have a low interfacial tension. That is, the surface tension of a soap solution should be thought of as the condition of the surface film, whether

in contact with air, with solids, or with fluids. In the last case, interfacial tension is the more accurately descriptive term.

When water is made to drop into oil the drops form with difficulty, the resistance at the interface resulting in few and large drops compared with the mass of water. This phenomenon indicates the high interfacial tension existing between water and oil. When soap is added to the water, the tension is lowered remarkably, and the soap falls into the oil easily in the form of fine drops. For instance, if a measure of tension between water and mineral oil is expressed as 35 dynes, a soap solution under the same circumstances may show a value of only 2 dynes. The difference between water and soap solutions may be shown simply by using pipettes with very small bores, which deliver drops of constant size under given conditions. Two marks at a certain distance apart may be made on the stem of the pipette, the pipette filled with distilled water, and the water allowed to pass out drop by drop into benzol, kerosene, or other mineral oil, or a vegetable oil. The drops are counted which pass out between the two marks on the stem of the pipette. In the same way, sample soap solutions may be run and compared in regard to the number and the character of the drops. The difference between the two will be evident. If, let us say, six drops of water pass out from between the marks, the same length of pipette stem will deliver four or five times as many drops of a soap solution. This means, in cleansing, that oil and soap sols mix readily, so that when the oil or greasy dirt is broken up into droplets by being mechanically agitated, another step in cleansing, emulsification, may readily ensue.

Emulsification of Grease

Emulsions in food and medicinal preparations are familiar occurrences, and are usually produced by fluid fats subdivided by mechanical agitation into minute droplets, as in mayonnaise, each droplet being kept from coalescing with its neighbors by an emulsifying agent. A colloidal solution, such as that made by egg, gelatine, or soap, is a film former, because of low surface tension and consequent viscosity of surface film of this type of material in solution. A soap film has the nature of an elastic skin; it is extremely ductile and will stretch without breaking around particles of greasy dirt in the clothing. Nothing is better than a colloidal soap solution as an emulsifying agent.

Three things are necessary in a cleanser if it is to emulsify fat. It must be in fluid form. Therefore body clothing must be washed in water at least of body temperature. There must be mechanical agitation, to break up the fat masses into microscopic particles. A soap which claims to cleanse by soaking or rinsing alone is therefore limited in its action. It must contain an emulsifying agent, to form a film around each droplet of fat which will keep it separate from all others so that it can be lifted and floated off by the buoyant power of soapsuds.

Langmuir[1] and Harkins[2] have developed a theory of the condition of the soap molecule in water which has a bearing on the structure of the oil-in-soap emulsion. The formula for a soap, e.g. $C_{17}H_{35}COONa$, shows that it is made up of a hydrocarbon chain, and a COONa grouping. The hydrocarbon chain is not soluble in water, but is soluble in fat. The COONa group is soluble in water, especially the sodium, but less so in fat. In the body of the soap solution, the effect of the opposed properties of solubility is a tendency of the hydrocarbon chains to come together to form what are called *micelles*, or *micellae*, leaving the COONa groups raying out into the water. In the surface of the solution the hydrocarbon chains are forced out into the air, leaving a concentration of soap molecules with the COONa groups in the surface film, the rest of the molecule crowded above the surface.

Now consider the case of oil and soap in contact. The action is reversed. The hydrocarbon chains enter the oil droplet, leaving the COONa grouping to encircle the droplet as they reach out to the surrounding water. This intersolution of oil and soap surrounded by part of the soap molecule creates a far more stable emulsion than if the oil and soap were in two distinct phases.

Sudsing Power

Since the surface of a soap solution has high viscosity, a soap film can stretch to make a soap bubble, and masses of soap bubbles make suds; the soap's ability to make suds is called its "sudsing power." The permanence of the suds is one sign that soap is performing its emulsifying action. It indicates live soap doing work. Suds is an emulsion of air enclosed in soap films or

[1] *Journal American Chemical Society*, 29 (1917), p. 1848.
[2] *Ibid.* 29 (1917), p. 354, 542: and 41 (1919), p. 970.

rather a double film, for a soap bubble is two films with a layer of liquid between. This enclosed air not only acts as a cushion to hold up the loosened dirt particles and prevent re-settling on the fabric, but it has a significant part in cleansing through aëration. Directions for laundering rightly emphasize the need for maintaining a moderately full suds during the washing operation. *Do not let the suds drop* should be a main thought in laundering. If the suds fall the dirt falls back also; washing long continued until the suds fall results in streaky garments from the deposition of dirt still more finely divided by the mechanical agitation of the washing process.

The reason for the exhaustion of soap solutions can be understood if we think again of the adsorptive process. If soap adsorbs particles of dirt, in a sense it is also adsorbed by them, and the result is not free soap but a conglomerate of soap and dirt. When all the soap is used up in this interaction, the suds disappear.

Chemical Action of Soap in Cleansing

Until colloid chemistry shed light upon the physical forces contributing to detergency which are to be found in a soap solution, the cleansing action of soap was supposed to be chiefly chemical, the result of the effect of either free alkali added to a soap, or alkali set free in a soap solution. From the moment a soap, even a so-called neutral soap, enters water, it ceases to be neutral and shows an alkaline reaction.

Ionization

As all students of chemistry know, ionization accompanies the hydrolysis or dissociation of the salt of a weak acid and a strong base, such as a soap is. It is an act of double decomposition, wherein water also decomposes into hydrogen and hydroxyl ions. If dissociation were simple and complete, we should have fatty acid and sodium ions from the soap, mingled with the hydrogen and hydroxyl ions of the water. That this is not the simple act of dissociation it was once thought to be, we have reason to believe. However, by the use of phenolphthalein or other indicators of alkalinity, we recognize the OH ions, and conclude that some dissociated alkali, NaOH, has formed.

This alkali was supposed to do most of the work of cleansing, through its neutralization of acid dirt, its combination with fatty

acids and greases in the clothing to make new soaps which could be washed away, and its slight emulsifying action. The advantage in employing a soap to provide this alkali, instead of using the direct solution, was explained by the fact that soap was recognized to yield it in a controlled way, whereas the effect of the undiluted alkali was immediate and harsh.

To a degree this is true, only the emphasis has shifted from the importance of the chemical explanation to the greater importance of the physical. Furthermore, the fact of hydrolysis and its release of alkali is looked upon as a drawback in most detergent operations. It is the effort of the soap chemist to combine constituents which shall create a soap in which hydrolysis is controlled to the minimum of alkalinity.

Theories have changed, a change which has been pointed out in regard to the states of the ionized material and the degree of hydrolysis in a water solution of soap. These theories relate especially to the behavior of the fatty acid radicals.

The fatty acid parts of the soap molecule are insoluble in water and do not behave like simple electrolytes. Because of their chemical nature, especially perhaps because of the existence of one or more double bonds, including that of the double-bonded oxygen in the COOH group, addition products are possible in the changes attending hydrolysis. The fatty acid groups may become hydrated by taking on OH groups; there is evidence that they combine with some of the released sodium to form acid soaps; there is also the micelle theory, which maintains that they form aggregations of micelles. Therefore the hydrolysis of a soap solution does not entirely mean a separation into free fatty acid and free alkali.

Due to this behavior of the fatty acid groups, the dissociation of a soap solution is small compared with the mass. J. W. McBain found that pure potassium palmitate in approximately 0.3 per cent solution at 90° C. hydrolyzed 6.8 per cent; sodium palmitate 6.6 per cent. In more concentrated solutions he found the hydrolysis lower, but in the same proportion.[3]

The degree of hydrolysis varies with the type of soap, not only with regard to the alkali used, as described above, but with regard to the choice of fat. Stearates or other soaps made from fats containing the higher saturated fatty acids hydrolyze to a

[3] *Journal American Chemical Society*, p. 105 (1914), p. 957; 115 (1919), p. 1279.

greater degree than those made from the lower acids of this series, or from the unsaturated vegetable oils. For instance, Castile soap made from olive oil, and coconut oil soaps show a low degree of hydrolysis, and a castor oil soap even lower. A cold-made soap does not hydrolyze to the extent of a boiled soap, a fact resulting from the restraining presence of glycerol in the former.

Temperature, and degree of dilution of the solution, make marked changes in the degree of ionization. The more dilute a soap solution, the greater its dissociation in proportion to the amount of soap. Increasing the temperature greatly increases the speed and amount of hydrolysis.

Since for certain laundry operations, especially the washing of woolens, conditions of least ionization are desirable, in addit ion to the choice of a mild soap made from an oil base, as indicated above, the temperature should be controlled to approximately blood heat, and the soap should be used in a concentration to make full suds. Conditions favoring ionization will release alkali which will be absorbed by the wool fiber, greatly to the detriment of the fiber.

Given a neutral soap, under controlled conditions of hydrolysis, the amount of dissociated alkali need not be considered under ordinary circumstances. Existing as it does, in equilibrium with some free fatty acids in the garment, it reacts with these or with ionized fatty acids to form soaps, but it is too dilute to saponify fats and greases themselves. Its emulsifying action is slight.

As to free alkali, either caustic or carbonated, so often a constituent of laundry soaps, it has its share in cleansing according to the cited functions of an alkali. It also exerts some buffer action, whereby the dissociation of the soap is stabilized. Sodium chloride, with its common sodium ion, also has this buffer effect, although its presence in a soap decreases its value as a detergent. The soap chemist must decide in a soap for a given purpose, what kind and how much of an alkaline builder is desirable on account of its buffer action, and how much more will increase total alkalinity beyond the point of efficiency and safety as a detergent.

The function and value of these alkaline builders of a crystalline nature are not at all settled questions. Some authorites contend that nothing takes the place of soap itself; that if these builders are added, any cleansing action which they show is shown because they are taking the place of a certain amount of soap of greater

detergent efficiency. (Fall: *Journal of Physical Chemistry*, June, 1927.)

Measurements of free and dissociated alkali in typical soaps are described in Chapter X. It is technically important to know within a close range the alkalinity of a soap for special purposes, such as shaving soap, soaps for washing wools and softening silks, automobile soaps, etc. The total alkalinity, that is, the sum of free and dissociated alkali in a soap sample, is best measured in terms of its pH value, or the concentration of hydrogen ions in its solution. This method of measuring has become familiar to all advanced students in chemistry. Taking pH_7 as neutrality, or equal concentration of hydrogen and hydroxyl ions, values higher than seven indicate alkalinity. A soap solution showing a value of pH_8 would be extremely mild and seldom found except as a specially prepared soap for a specific purpose. Values of pH_9 to pH_{10} are commonly found in mild soaps for washing fine fabrics, that is, alkalinities equivalent to a range between N/100,000 NaOH and N/10,000 NaOH. Soaps for more general laundry purposes may show a range of fractions between pH_{11} and pH_{12}, or alkalinities of N/1000 to N/100. These would be built-up soaps or soaps containing free alkali.

Summary of Cleansing Action

To summarize the explanations of the cleansing action of soap, we have seen that we are dealing with a combination of physical and chemical forces, of which the physical, as attributes of a colloidal state, offer a far more satisfactory reason for phenomena of detergency than that found in chemical action alone. These physical properties of a soap solution—low surface and interfacial tension, and consequent power to spread and penetrate; Brownian movements to dislodge and peptize dirt; surrounding, adsorption, emulsification, by which to hold on to the dirt, and the floating off action of buoyant suds—are properties which are so truly characteristic of no other substance in solution, and which give to soap its rank as the greatest of detergents.

CHAPTER VII

TEMPERATURE

Factors Controlling Optimum Temperature

In the preceding chapters frequent mention has been made of temperature in connection with the various cleansing operations. It is a subject which is not any too well understood by the average user of soap, and its importance warrants special attention.

The temperature to be used in a cleansing operation is sometimes never considered, sometimes vaguely adjusted, seldom determined definitely in relation to the influencing factors in the case. These factors include:

1. The nature of dirt or stains in the clothing.
2. The nature of the fabric.
3. The dye.
4. The soap.
5. The need for sterilization.

The Nature of Dirt or Stains

What part does the nature of dirt or stains play in the cleansing operation? Suppose the cleansing operation is the typical family wash. All the above factors may present themselves, but one of the first considerations is the question of the kind of dirt or stain which may be present. If these are protein in nature—egg, blood, milk—and we put the stained article directly into hot water, the stain is fixed in the fabric. It does not take the boiling temperature to cook an egg. Body soil containing perspiration or other excretions, some mineral stains, and some fruit stains are also made more difficult of removal by first placing in hot water. Soaking in cool water preliminary to washing loosens or removes many such stains.

A safe temperature for soaking clothes before washing is that of the room, and never above 90° F.

The Fabric

Where wool, silk, and most synthetic fabrics are concerned, the question of temperature becomes paramount. The deteriorating effect of heat alone on wool and silk has been noted, also that of heat as an accelerator of chemical action between alkali and fiber. Some synthetic filaments stand heat very well, others are much weakened by heat; a good rule for all is the safe one of moderate temperature.

The safe temperature for washing wool, silk, and synthetic fibers is close to body heat, or about 100° F. This temperature will keep body fats and oils in a fluid condition, therefore rendering them easily removable. For soiled garments, to offset such a moderate temperature, use two soapy waters, which is a good rule in all washing. Keep the rinse waters at the same temperature as the wash waters.

The Dye

Heat expands, and in expansion, may dislodge dye molecules. It may also by chemical change decompose and destroy the dye. Colors which are fugitive in hot water are often quite satisfactorily washed in cool water. Heat also increases chemical action between soap and dye, especially noticeable in the case of acid dyes on wool and silk, which, being affected by alkalies, are susceptible to the action of soap in hot water. If there is any question about the ability of a dye to stand up under proper washing, it would be foolish to wash it without a preliminary test. Certain dyestuffs are almost fade-proof under any treatment—hot water, strong soaps, even bleaches; others, and still the majority, are not so dependable. If intelligently handled, however, which means low temperature, mild soap, quick treatment, no friction, and proper method of drying, almost any color can be washed.

The safe temperature for washing colored fabrics is from 90° to 100° F. Where the dye will stand the hotter water which may be necessary for very soiled garments, keep below 120° F. as a rule.

The Soap

Having no other consideration in mind for the moment except the soap, how hot should its solution be for efficient action? Will a tallow soap and an olive oil soap work equally well in waters of different temperatures? This is an important question in detergency, but a difficult one for the consumer to answer.

No doubt every type of soap has its optimum efficiency at a certain temperature of solution, the point where it is most completely in the colloidal or hydrosol state, and least in true solution. This is almost entirely a matter of temperature control, given the strength of solution usual in most washing operations. But optimum temperature conditions may be degrees apart with soaps of different composition.

The reason for these differences is found in the nature of the fatty base used in the composition of the soap, and an index of the behavior of any soap in this respect is found in what is called the titer of the fatty acid content. The titer of a fatty acid is the point on the centigrade scale (the usual expression) at which it will solidify. That is, it is the critical point of change from liquid to solid, or vice versa. For example, oleic acid, a chief constituent of olive oil, has the low titer of about 8° C., and is liquid above this point. It follows that an olive oil soap is a cold water soap, showing efficient colloidal solution in water in which a soap made chiefly from stearic acid would fail to dissolve or make suds. For stearic acid has a titer of about 70° C., therefore in a soap it would require a temperature of about 160° F. for efficiency; whereas an olive oil soap shows its best sudsing power about room temperature, and at 120° F. or above passes into true solution, loses its suds, and is likely to deposit dissociated fatty acids on the clothing.

The so-called cold water soaps are made from fats containing a preponderance of low titer fatty acids. They are efficient in temperatures from 70° to 120° F., and are adapted to the washing of wools, silks, synthetic fibers, and dyed fabrics. They should not be used in water hotter than the range indicated. Toilet soaps and semi-toilet soaps designed for fine fabrics, are usually in this class. Cold water soaps are often recommended for dishwashing, because of the mild effect on the hands, but if used for this purpose the water should be at a temperature suitable for the hands. If scalding water is used in a dishwashing machine, a different type of soap is required for complete suds formation.

Fortunately for soapmaker and consumer alike, natural fats even of the beef tallow kind contain a certain proportion of low titer fatty acids, which modify the physical nature of the fat accordingly. The resulting titer, however, is not an average of the combined titers of the fatty acid components. For instance, pure

stearic acid and pure palmitic acid, the first with a titer of about 70° C., and the second about 63° C., when mixed in equal proportions show a titer of about 55° C. Nor is the melting point much lower when palmitic and oleic acids are likewise mixed.

Soapmakers consider that a soap with a titer of about 40° C. gives good results in water between 120° and 160° F. If such a soap were made from palmitic and oleic acids, the proportion of palmitic to oleic would need to be about 1:3. The average laundry soap for general use shows a titer in the neighborhood of 40° C.

Hillyer has made a comparison of the efficiencies of different types of soaps in cold and hot solution, using interfacial tension measurements as the criterion. (*Journal American Chemical Society*, 1903, 25, 1262.) His standard solution for hot water soaps was a pure sodium palmitate, giving an average of 268 drops from the pipette used. For cold water soaps he used a pure sodium oleate, with an average of 153 drops from the pipette. Comparing certain commercial soaps with these standards, he found considerable variation in efficiency in different types. For instance, a steam laundry tallow soap had a drop number of 104 and an efficiency rating of 30 in cold water, while in hot water the drop number was 277, greater than the sodium palmitate standard, and the efficiency rating 106. A cold water coconut oil soap had a drop number of 121 and an efficiency rating of 37 in hot water. As a rule, the decline in efficiency of cold water soaps used in hot water was less than that of hot water soaps used in cold water. Among the hot water soaps no standardization of efficiency was found, as gauged by this one test, laundry soaps of this type ranging in efficiency ratings from 19 to 49 in the cold water, and from 35 to 106 in hot water.

How shall the consumer know what is the optimum temperature for a given soap? As a rule, cold water soaps can be recognized by their advertised uses, and likewise the typical laundry or hot water soap.

> *The optimum temperature of a soap solution is approximately that at which it shows its fullest sudsing action.*

The temperature of the first rinse water is important, since this contains so much soap carried over from the suds. If it is considerably hotter than the last wash water, it will hydrolyze the dilute soap it contains, and kill the suds, an action which opens a possibility for deposition of fatty acid or acid soap on the clothing.

If much colder than the wash water, it may prevent the solution of soaps with a titer around 40° C. This would be equally unfortunate for the clothing.

The best temperature for the first rinse water is that of the last wash water.

If a bleach is used either in the soap solution or afterward, temperature must be considered. As a rule, bleaching is a process of oxidation not unlike the burning of fuel, except in degree. Combustion can be speeded up, or reduced to an immeasurably slow process. The oxidation of bleaching is increased by temperature even more than by a strong solution of the bleach. Lest we burn our fabrics almost as if they were held in the gas flame, let us restrain the oxidation by lowering the temperature.

Commercial laundries use a temperature range of 120° F. to 160° F. for bleaching, but those run on scientific principles know more accurately than the housewife just how much free chlorine is being utilized, and how many minutes should be given to the action. Not all laundries, however, show care in this process, for, as has been pointed out, it is a frequent experience to have white goods come home from a laundry with all the marks of over-bleaching. A brittle feeling characterizes over-bleached material, and decomposition soon follows.

A safe temperature for home bleaching is about 68° F. Ten minutes in a solution of moderate strength should be sufficient; if the temperature approaches 120° F. allow only five minutes.

Since both temperature and time should be controlled in bleaching, it is poor policy to use free bleach in the wash water.

The Need for Sterilization

A conviction of the necessity for boiling clothes in order to get them perfectly sterilized still lingers in the mind of many a home laundress, so that in spite of the arduous labor involved, the wash boiler gets its weekly quota of bed linen, handkerchiefs, shirts, towels, and other articles of cotton or linen. Does this operation sterilize clothing, and is it necessary in order to effect sterilization?

We have seen that soaps lose their principal cleansing power when they leave the colloidal state and go into true solution in boiling water; that at this temperature chemical action between alkali and clothing is greatly increased, with a deteriorating effect on fabric strength especially if air has free access to the clothing.

This much of detergent value is lost, then, at the boiling temperature, and even a certain sterilizing action ceases, for soaps in the colloidal state have a selective effect on bacteria which is lost when they leave that state.

Generally speaking, ordinary temperatures employed in the laundry operations are sufficient to provide for thorough cleansing and disinfection of clothing under normal conditions. This subject receives further attention in the chapter which follows. When the need of special sterilization arises, then the wash boiler serves a useful purpose. Very few non-spore-bearing bacteria survive the temperature of boiling water for even a few minutes; very few spore bearers are found on our clothing, so boiling may be considered a safe method of sterilization except under unusual circumstances requiring expert advice.

A further disadvantage of the boiling of clothes results when they are removed from the boiler and enter a tub of water at lower temperature, in which soap decomposed in the hot solution may be precipitated as a greasy deposit on the garment.

As has been seen, this question of temperature is a many-sided one, and here, as in cooking, the housewife will often find that the use of a thermometer will help to standardize laundry methods and take the guesswork out of many an operation.

Considering the kinds of fabrics in vogue to-day, and their frequent fine quality, it can be surmised that most errors in temperature lie on the side of too high heat. Stains may be set, wool may shrink, silks and synthetics may weaken, colors may fade, bleaching may spell destruction, and even cleanliness itself may be defeated through killing the suds and decomposing the soap.

CHAPTER VIII

ANTISEPTIC VALUE OF SOAP

Relation of Soap to Cleanliness and Civilization

Without cleanliness in our modern life there is little health; without soap there is little cleanliness. When we think of the germs with which we come in contact every second of the day in our crowded environments, the subway straps we grasp, the people who jostle us, we turn to soap and water with a feeling of reliance, and are grateful to the civilization which has spread the doctrine of health through cleanliness.

There is a sharp contrast between our modern knowledge of the value and uses of soap and the ignorance and lack of it in the dark ages, ages dark indeed so far as cleanliness was concerned. In those days skin diseases, lesions, and ulcers were of common occurrence, and epidemics were frequent and virulent. Even among the well-to-do, and as late as 1665, as shown in the *Diary* of Samuel Pepys, bathing was an event. He writes: "My wife busy in going with her woman to a hothouse to bathe herself, after her long being within doors in the dirt, so that now she pretends to a resolution of being hereafter very clean. How long it will hold I can guess."

The same organisms are present every day among us which wrought havoc so often to whole communities in the dark ages. Bacilli by hundreds of thousands find lodgment on the skin, and by hundreds of thousands are removed by soap and water.

Are Soaps Antiseptic?

Whether all soaps, or specific soaps, have the power to kill as well as mechanically remove disease germs on skin and clothing, is an important question, especially when contagious disease enters the household. Authorities present conflicting answers to this question, and it is clear that a yes or no answer cannot be given. Much depends upon the type of organism which the soap is called upon to combat; the temperature and the concentra-

tion of the soap solution; and to a certain degree, on the kind of soap.

Authorities Quoted and Personal Investigation Cited

It has seemed best to lay before the reader a digest of the opinions of some leading investigators as well as to cite personal investigation, rather than to draw arbitrary conclusions.

The Cleanliness Institute in New York City, founded to teach and spread the doctrine of cleanliness, and incidentally to increase the consumption of soap, lays down the principle that every unclean person is a potential center of infection, and a menace to the community. The following excerpts are taken from its collected bibliography:

Rosenau's *Preventive Medicine and Hygiene*, p. 1369: The value of soap consists in the removal rather than the killing of germs; that is, the cleansing properties are more important than the germicidal action. In hand-washing, all the bacteria are not removed by soap and water, and the exposure is not long enough nor the concentration strong enough to disinfect. As bacteria and spores do not propagate on soap, the danger of infection from using bar soap is remote.

Meredith's *Hygiene*, p. 519: The medication of soap is not very successful. No soap is much more curative of skin disease than any other. They cannot contain enough disinfectant chemicals to make a sufficiently powerful solution in water. The removal of dirt is about all that can be expected, and that is a great deal. The advantage of medicated soap is that it encourages the use of soap itself. If one thinks it has powerful properties, more of it is likely to be used. Since soap itself is not germicidal, the bacteria that get on it may remain alive. It is therefore imperative to use only one's individual soap, or that from a container of liquid or powdered soap.

Soap Gazette and Perfumer, vol. 30, p. 85, Mar., 1928: The value of cleanliness as an ally in preventing infection may be judged by a careful test of hand-washing, made during the winter months when respiratory diseases are most prevalent. The average man, washing his hands in warm, clear water, contributes about 1,600,000 organisms from that source alone. In warm, soapy water his contribution rises to 4,000,000 organisms. This indicates that soapy water is more than two and a half times as effective as warm water without soap.

Reasoner and Gill, "The Use of Soap in the Prophylaxis of Vincent's Infections" (*Journal of the American Medical Association*, vol. 88, pp. 716–719, Mar. 5, 1927): Solutions of ordinary toilet soaps, as well as pure soaps prepared in the laboratory, have a selective action on this class of organisms (Vincent's spirochete), and a definite spirocheticidal effect, and their use in dentifrices assists in keeping the oral cavity free from mouth spirochetes, thereby affording a measure of protection against tissue infection. The presence of the organisms of this disease and of the disease itself vary inversely with the care given to

personal hygiene and the regular use of soap by the persons concerned. Any measures that retard or prevent chronic irritations of the mouth will doubtless have some effect in lowering the incidence of cancer of the mouth. The proper use of soap compounds is rather that of a prophylactic than a method of cure, and their use for the latter purpose is not recommended.

Reasoner, "Ulcerative and Gangrenous Balanitis" (*New York State Medical Journal*, July 15, 1927): In 1916 a report was made upon the marked spirocheticidal effect of soap solutions upon *Treponema pallidum*. It was found that a 0.1 per cent solution of the ordinary toilet soaps, when floated under the cover glass of a slide of *Treponema pallidum* undergoing examination, caused their immediate death and dissolution.

And from other sources:

In the 1917 *Yearbook of Pharmacy*, London, Churchill, p. 190, in "Soap as a Wound Dressing," Ratynski speaks highly of the value of soap solutions as a dressing for wounds. "A twenty to forty per cent solution of white Castile soap in warm water is prepared, in which sterilized gauze swabs are dipped and used to cleanse the surface of the wound; this is then freely irrigated with the soapy water, and covered with layers of gauze saturated with soap lather. The soap solution has only feeble bactericidal powers, but it has soothing, cleansing properties, does not coagulate the blood, softens scabs, and by stimulating exosnosis, causes a flow of wound secretions from within outwards."

There is no doubt that in general the germicidal value of medicated soaps is low. The germicide may be so dilute as to be useless; it may have volatilized anywhere from the crutcher which mixed it in the soap, to the user; it may be chemically changed or rendered inert by the soap itself. Concerning such soaps we find:

Rideal, E. and S., *Chemical Disinfection and Sterilization* (London, 1921): The efficacy of many disinfectant soaps as germicides is small, partly because it is seldom that disinfectant soaps are tested properly as to their germicidal action upon specific organisms under conditions which approximate their use in practice, and partly owing to the fact that there are many disinfectants which have valuable properties as such, but which are totally unfitted for use in conjunction with soaps. The conditions which obtain when a disinfectant soap is used are very different from those of ordinary disinfecting. As the time of contact is short, so it is necessary that the proportion of the active ingredient should be high. Again, unless the disinfectant employed is readily soluble in water, actual contact of the infected parts with the disinfectant cannot be attained in the limited time given in washing. In coal tar soaps and those containing oils which are not very soluble in water, although the disinfectant is emulsified by the soap, the actual laving of every part of the infected area by the active ingredient for the necessary time to effect the death of the microörganism is by no means certain. Organisms differ very markedly in their resistant power. Many of them form spores which are especially difficult to kill, so that even

when a soap contains an approved disinfectant, the latter must be present in quantity above that required for the fatal dose for the most resisting spores.

Harrington, C., *Practical Hygiene*, p. 597, 1911: Compared with ordinary soaps, medicated soaps appear to be of doubtful utility, although in the hands of some experimenters they have yielded good results. From an extensive investigation of these soaps, Symes (*Bristol Medico-Chirurgical Journal*, Sept., 1899) concluded that, for all practical purposes, most of them possess no added value, but that the mercury soaps are useful in disinfection of the hands. A one per cent solution of the biniodide soap killed pus cocci in one minute, while the other soaps failed to do so in three hours. Nijland (*loc. cit.*) found that the addition of disinfectants to soaps increases their action in some cases and diminishes it in others, the latter especially when the added substance combines with the ordinary constituents. According to his experiments, the most powerful of all is the corrosive sublimate soap, which, however, has less power than the corresponding amount of sublimate alone. . . . Concerning carbolic acid and cresol soaps, the weight of evidence is clearly in support of the assertion that they are in no way superior to common soaps. Many contain no more than sufficient to make them powerful in odor, which is not sufficient to confer any marked bactericidal power.

Jolles, *Zeitschrift für Hygiene und Infectionskrankheiten*, vol. XIX p. 130, 1895: "It must be remembered that soaps themselves have considerable antiseptic power. In the case of typhoid bacilli the disinfection is more marked at 4° to 8° C. than at ordinary or higher temperatures. A one per cent solution was injurious to the germs in fifteen minutes, and a six per cent resulted in their entire destruction. A three per cent solution was fatal in one hour, and a one per cent in two hours. B. coli communis was less easily destroyed; at low temperatures a two per cent was fatal in six hours. There is no doubt that prolonged contact with soap rendered surfaces practically sterile, but under ordinary circumstances ordinary soap fails to be effective." The soap that Jolles used was practically neutral, containing only 0.041 per cent of free alkali. His general conclusion was that, as shown by his tests on other forms of bacteria, soap is particularly valuable and adaptable to its ordinary use in washing dirty and perhaps infected clothing.

Serafini (*Archives für Hygiene*, vol. XXXIII, p. 369, 1899) found that in the ordinary washing of clothes soaps have little disinfecting action, whereas other investigators, such as Behring, Konradi, and Rodet, find more or less germicidal power.

This conflicting evidence emphasizes the fact that not all soaps are equally germicidal, nor is the same soap destructive in the same degree with different varieties of bacteria, but it does establish the fact that under certain conditions soap has a bactericidal action, in addition to its certain property of removing mechanically large numbers of microörganisms from the area of contact.

As to the first of these facts, some personal experiments in the bacteriological laboratory of Teachers College, Columbia

University, showed that a commercial product containing soap, carbonated soda, and a perborate bleach destroyed typhoid bacilli, if the soap product in one-half of one per cent solution was in contact with the bacilli at 104° F. for three hours. As this is not a stronger solution than is often used in home laundering, such a product would be effective in sterilizing infected clothing in a typhoid case, under the conditions described. Security might be felt, however, if the clothing were soaked overnight in a tub of water containing one and a half cups of such a product in solution. This test repeated with a practically neutral soap chip type, and again with a silicated soap, gave only slight turbidities in a twenty-four-hour incubation in broth, showing that these soaps had considerable germicidal action toward this particular bacillus; whereas a granulated soap, containing a high percentage of carbonated soda but no bleach, was not nearly so efficient. When plated, the colonies in the latter case were approximately in the proportion of thirty to one of the pure soap or silicated soap inoculation.

In this comparison between a carbonated soap and pure and silicated soaps, it is indicated that the difference in colloidal nature and degree of surface tension with consequent adsorptive power furnishes an explanation of the greater germicidal efficiency of the pure and silicated forms. Both of these contain more material in colloidal form and have lower surface tensions than the carbonated soap.

Surface tension is conceded to have considerable influence on germicidal efficiency. If the surface tension is low, there is a concentration of the disinfectant in the surface film, in close contact with the suspended bacteria. The same colloidal properties evidenced by soap solutions toward dirt, may be considered to apply to their action toward bacteria—adsorption, film formation around the organism, possibly solution and destruction, as well as mechanical removal. The hydrogen ion concentration of a soap solution and different forms of organisms also have a bearing on germicidal action.

One of the newer germicides to appear on the market, a solution in a glycerol-water mixture, has a surface tension of 37 dynes, which brings it almost in the class of a soap solution so far as surface tension goes. This low surface tension is a factor in its germicidal power, according to tests cited by additional authorities.

Eggerth (*Journal of Experimental Medicine*, Baltimore, vol. 50, Sept. 1, 1929) cites experiments to prove that the alpha-hydroxy soaps exhibit high germicidal action toward certain organisms. As with other soaps, the germicidal action increases with molecular weight to a maximum, and then diminishes. The pH affects the germicidal action as it does with other soaps. The effect of the OH group in saturated soaps is to increase selective germicidal action; the effect in an unsaturated soap is to diminish it.

Hampil, "Effect of Pure Soaps on Bactericidal Properties of Phenolic Germicides" (*Journal of Bacteriology*, vol. XVI, p. 267, Nov., 1928): The results of experiments by Hampil indicate the impossibility of producing a germicidal soap by adding small quantities of a phenolic compound to soap. The addition of large quantities is not feasible, as the cost of production precludes the use of any but very crude and irritating phenols. Therefore phenols are unsuitable as disinfectant agents in the production of germicidal soaps. Evidence shows that soap removes the phenolic system from the solution and thereby interferes with its bactericidal activity, since this activity is dependent solely on the solution of phenol in water.

Several investigators have studied the effects of special soaps such as sodium ricinoleate upon bacteria and toxins:

Kozlowski, "Comparative Study of the Action of Sodium Ricinoleate upon Bacteria" (*Journal of Bacteriology*, vol. XVI, pp. 3, 203, Sept., 1928): Microorganisms investigated: Streptococcus viridans (No. 13), S. pyogenes (No. 12), S. equinus (No. 17), S. lacticus (No. 1B), S. fecalis (No. 16). Conclusions: Streptococci isolated from cases of erysipelas, measles, and scarlet fever most susceptible to bacterial action of sodium ricinoleate. Killed in this soap solution in a dilution of 1:5000 in about seven hours, or sooner at 35° C. In a control culture without soap they survived for more than one week. Their growth was inhibited by this soap in a dilution of 1:2000 or less. In cellular susceptibility they approach that of pneumococci, which are killed by the same soap under similar conditions in a dilution of 1:1000. Pneumococci are dissolved quite readily by sodium ricinoleate in a dilution of 1:5000; in this regard they differ from other bacteria investigated.

Of the bacilli, B. diphtheriae are quite susceptible to the inhibitory, much less to the bactericidal action of sodium ricinoleate. B. tuberculosis is slightly susceptible; inhibited in growth by the soap in a dilution of 1:2000. B. paratyphosus, B. dysenteriae, B. coli communis and S. fecalis are quite resistant to inhibitory and bactericidal action of sodium ricinoleate. S. lacticus, S. pyogenes and S. viridans are inhibited in growth by sodium ricinoleate in a dilution of 1:5000 or lower, but not killed in a dilution of 1:100. The bactericidal effect of sodium ricinoleate is conditioned by the specific cellular susceptibility of bacteria, and further by the concentration of the soap solution and by the time and temperature of exposure.

Netter, Andre, Cesari and Cotoni, "Action of Sodium Ricinoleate on Bacteria and Toxins" (*Chemical Abstracts*, vol. 21, p. 1288, 1927): In the tests virulent cultures were mixed with equal volumes of a 0.2 per cent solution of sodium ricinoleate. Rabbits which received a subcutaneous injection of 1 cc.

of a ricinoleated pneumococcus culture were not affected, but those receiving 0.5 cc. resisted inoculation from a virulent pneumococcus culture for twelve days. Smaller doses did not prevent inoculation but prolonged life three or four days as compared with the control animals. 0.1 cc. of the serum of rabbits which had received the ricinoleated culture twice at twelve-day intervals neutralized at least six fatal doses of the virulent culture. Similar results were obtained with a ricinoleated culture of virulent streptococci, except that larger doses of the culture were necessary.

Ricinoleated soaps contain ricinoleic acid, a hydroxy acid found in castor oil. Dr. Forrest R. Davison's researches (*Journal of Infectious Diseases*, vol. 43, pp. 292–9, 1928) confirm the efficacy of a castor oil soap, and add testimony as to the germicidal value of other soaps made from certain oils. From his work the following summary is taken:

Several soaps were found effective against streptococcus hemolyticus in the following germicidal rank: Castor, coconut, linseed, cottonseed, and olive. Against streptococcus viridans the order was: Castor, coconut, linseed, apricot, and cottonseed. Against staphyloccus, they ranked: Castor, cottonseed, coconut, olive, and corn oil. Averaging the results with the three organisms, castor oil soaps showed greatest bactericidal power, with coconut oil soaps second with two, and fourth with the third. Next come linseed and cottonseed oils.

Other investigators have found that coconut oil soaps are particularly effective against the typhoid bacillus. M. A. Reaoner, Lieutenant-Colonel U. S. Army Medical Corps, writing for *Soap*, December, 1927, says:

"The oleates, laurates, linolates and linoleates have a lesser degree of selective activity on the pneumococcus, streptococcus, meningococcus, and gonococcus, and do not affect the bacillus of typhoid. Coconut oil soaps have a pronounced action on the typhoid bacillus as well as on the paratyphoid A and B bacilli and bacillus dysenteriae of both Shiga and Flexner, and may be said to have the highest germicidal action of any." He quotes Walker (*Journal of Infectious Diseases*, vol. 35, p. 557, Dec., 1924; vol. 37, pp. 181–192, Aug., 1925): "He conducted a series of experiments showing conclusively the germicidal action of soap solutions on the bacteria found in saliva. The bacillus of diphtheria is affected about as are the pneumococcus and streptococcus. Lauric acid soap was shown to have the most general action as a germicide, and it is this acid which is found in greatest proportion in coconut oil. A solution of 1:50000 was sufficient to kill the pneumococcus in fifteen minutes, and a 1:3000 killed the streptococcus, and one per cent the typhoid bacillus in the same length of time.

"It seems probable that the bactericidal as well as the spirocheticidal action is in some way concerned with the well known effect of soaps in lowering the surface tension of water. However, this does not explain such selective actions

as were shown to exist, as well as the resistance of the staphylococcus. It is suggested by Walker that this may be explained by the variations in interfacial tension between the liquid and the bacterium, and that this tension varies with the liquid-air interspace.

"In some investigations carried out by us on the spirocheticidal action of these various soaps, the results obtained were practically in accord with those reported by Nichols and Walker. The stearates showed little activity, while the oleates were more effective. Ittner explained this slighter action of the stearates by the fact that they are considerably less soluble. McBain has disproved the opinion formerly held by some that the germicidal action of soaps is due to the presence of free alkali. Walker's work, as well as part of that done by us, was performed with neutral soaps prepared in the laboratory from chemically pure fatty acids."

Performance of a Liquid Laundry Soap (Technologic Paper No. 273, Bureau of Standards, Department of Commerce, Washington, D. C.): The results of a bacteriological examination show that a liquid laundry soap (oil-potash soap containing about fifteen per cent organic volatile solvent and about twenty-five per cent anhydrous soap, no free alkali or insoluble matter and only traces of carbonated alkali) kills B. typhosus in ten minutes in dilution 1:5.

In *Sanitary Standards for Home Laundering*, by Balderston, Wilson, and Harris (Bureau of Publications, Teachers College, Columbia University) the authors state that a temperature of 149° to 158° F., maintained for twenty minutes in a closed vessel, is amply sufficient to destroy all pathogenic non-spore-bearing forms. Their experiments showed that B. coli were removed from the fabric in washing with neutral soap chips and modified soda, but were present in the wash water. Thorough rinsing was obviously necessary, and if the purpose of rinsing is to free the clothing most efficiently from the organism the first rinse should be in boiling water. Two suds washings were recommended.

Few non-spore-bearing organisms are able to withstand the boiling temperature for even a few minutes. Fifteen minutes' exposure to the boiling temperature destroys spores of most varieties of bacteria, but others resist for hours. Ten to thirty minutes' exposure at 60° C. kills cholera, spirillum, streptococcus, and typhoid bacilli.

Levine, Peterson, and Buchanan have investigated the germicidal efficiency of sodium hydroxide and sodium hydroxide-carbonate solutions, on a spore-forming organism of the subtilis group, at the same hydrogen ion concentration (*Journal of Industrial and Engineering Chemistry*, Jan., 1928). In the discussion at the close of the paper they say in part:

At a constant temperature and H-ion concentration (determined at 30° C.) sodium hydroxide and hydroxide-carbonate mixtures were not equally efficient germicides. At pH 13.18 to 13.20 and a temperature at 50° C. the commercial

alkali (a washing compound containing sodium hydroxide and carbonate) killed in 34 minutes, the sodium hydroxide in 40.8 minutes, and the hydroxide-carbonate mixture in 43.7 minutes—a variation of 22.6 per cent in killing time.

The titratable alkalinity was also unsatisfactory as an index of relative disinfecting power, for the 0.5 N hydroxide was less efficient than one of the 1.0. N hydroxide-carbonate mixtures, but more efficient than the other. . . . If the commercial alkali is compared with the hydroxide-carbonate mixture, it will be noticed that they had the same reaction (pH) and were both normal alkalies by titration, but the killing times were very different—namely, 34 and 43.7 minutes, respectively. Evidently neither the total alkalinity nor the H-ion concentration alone is a direct measure of the germicidal powers of these alkalies. Other factors are involved.

It is conceivable that the undissociated sodium hydroxide, rather than the OH ion, penetrates the bacterial cell. In this case the concentration of undissociated sodium hydroxide becomes the determining factor in the germicidal efficiency of alkalies. The addition of sodium carbonate to the hydroxide would result in an increase in the concentration of undissociated sodium hydroxide and thus increase the germicidal action. Because of the difficulty of measuring H-ion concentration at this high alkalinity, the change due to the addition of the carbonate would not readily be detected. . . . Herein lies a most serious obstacle in attempting to evaluate germicidal efficiencies of alkalies on a pH basis.

Eggerth (*Journal of Experimental Medicine*, vol. 50, p. 299, 1929) found that the germicidal action of soap is influenced by the pH, but that this manifests itself variously according to the length of the carbon chain. Thus soaps containing twelve and fourteen carbon atoms showed maximum efficiency when the reaction of the soap is acid, and were most germicidal toward gram-negative organisms; while soaps containing sixteen and eighteen atoms showed a higher germicidal efficiency when the reaction is alkaline, and toward gram-positive organisms.

The Cowles Detergent Company, of Cleveland, Ohio, in their bulletin entitled *Temperature, or the Influence of Heat on Washing and Sanitation*, give a most interesting report of a series of tests designed to measure the bactericidal action of certain washing compounds used in the cold process, where neither heat nor bleach add to the germicidal effect. Their own product, which contains a silicate, is indicated by "X" in the quotations from this report which follow:

In the tests here reported measured quantities of the following solutions, and an active culture of the spore-bearing organism B. subtilis were mixed. Thirty minutes at room temperature were allowed for the solution to kill the organism. The thirty-minute period is about the average for a suds operation.

After a thirty-minute period, a sample of the mixture was added to bouillon and allowed to incubate for twenty-four hours at a temperature of 37 C°. When tested after this period of incubation, to determine whether or not the detergents had shown sufficient bactericidal action to kill the bacteria, the following results were shown:

Test No.		Action on Bacteria	Condition of Bacteria
1.	.02% soap solution (92% tallow soap)	None	Alive
2.	.10% caustic soda (76%)	None	Alive
3.	.10% X	None	Alive
4.	.10% soda ash	None	Alive
5.	.10% modified soda	None	Alive
6.	.04% soap	None	Alive
7.	.16% caustic soda	None	Alive
8.	.16% X	None	Alive
9.	.16% soda ash	None	Alive
10.	.16% modified soda	None	Alive

In the following tests, Nos. 11 to 28, soap was built with various commonly used builders to determine their influence on the bactericidal action of soap. Note that carbolic acid (3%) will kill these cultures in this length of time:

Test No.		Action on Bacteria	Condition of Bacteria
11.	.02% soap plus .10% caustic soda (76%)	None	Alive
12.	.02% soap plus .10% X	None	Alive
13.	.02% soap plus .10% soda ash	None	Alive
14.	.02% soap plus .10% modified soda	None	Alive
15.	.04% soap plus .15% caustic soda (76%)	None	Alive
16.	.04% soap plus .15% X	None	Alive
17.	.04% soap plus .15% soda ash	None	Alive
18.	.04% soap plus .15% modified soda	None	Alive
19.	.15% soap alone	None	Alive
20.	.25% soap alone	None	Alive
21.	.12% soap plus .12% caustic soda (76%)	None	Alive
22.	.12% soap plus .12% X	None	Alive
23.	.12% soap plus .12% soda ash	None	Alive
24.	.12% soap plus .12% modified soda	None	Alive
25.	.20% soap plus .10% caustic soda	None	Alive
26.	.20% soap plus .10% X	None	Alive
27.	.20% soap plus .10% soda ash	None	Alive
28.	.20% soap plus .10% modified soda	None	Alive

From the above it is apparent that none of the washing solutions have any bactericidal action on the spore-bearing organisms under the conditions of temperature and time used in the tests.

The action of solutions used in the above tests was then investigated with respect to non-spore-bearing organisms. A culture of B. Coli was used, a series of active cultures giving the following results:

Test No.		Action on Bacteria	Condition of Bacteria
29.	.04% soap alone	None	Alive
30.	.04% soap plus .17% caustic soda (76%)	None	Alive
31.	.04% soap plus .17% X	Slight	Some killed
32.	.04% soap plus .17% soda ash	None	Alive
33.	.04% soap plus .17% modified soda	None	Alive
34.	.08% soap alone	Slight	Some killed
35.	.15% soap alone	Moderate	More killed
36.	.22% soap alone	Complete	All killed

Experiment No. 31 expresses a difference between the action of "X" and other alkaline soap assistants, and experiment No. 36 indicates that a concentration of about 0.22% is required to effect complete bactericidal action on the non-spore-bearers. This strength is greater than that used in the wheel for washing operations.

Carrying these tests still further, with incubation for a 48-hour period, we have:

Test No.		Action on B. subtilis	Action on B. coli
37.	.11% soap plus .22% caustic soda (76%)	None	Complete
38.	.11% soap plus .22% X	None	Complete
39.	.11% soap plus .22% soda ash	None	None
40.	.11% soap plus modified soda	None	None
41.	.15% soap plus .28% caustic soda	None	Complete
42.	.15% soap plus .28% X	None	Complete
43.	.15% soap plus .28% soda ash	None	None
44.	.15% soap plus .28% modified soda	None	None
45.	.15% soap plus .05% caustic soda	None	Moderate
46.	.15% soap plus .05% X	None	Complete
47.	.15% soap plus .05% soda ash	None	None
48.	.15% soap plus .15% modified soda	None	None

The conclusions drawn from these tests by the investigators are:

That in concentrations similar to those used in washing, only "X" and soap showed ability to kill completely the non-spore-bearers.

Complete extermination of non-spore-bearing bacteria is brought about by a solution of soap which is *built very strongly* with caustic soda. The required strength of caustic to bring this about, however, would be greater than is permissible in washing clothes.

No bactericidal action is shown by the carbonated alkalies, soda ash or modified soda. Moreover, when these alkalies are used as soap builders, they actually destroy the bactericidal action of the soap itself. In experiments 34, 35, and 36 the effect of soap solutions is shown to vary in proportion to the strength of solution, while in experiments 39, 40, 43, 47 and 48 it is shown clearly that the addition of soda ash or modified soda destroyed this action of the soap. A partial confirmation of the above is found in Lamborn's *Modern*

Soaps, Candles and Glycerin, p. 376, where it is stated that "hardwater or other soap precipitants lessen the disinfecting action, as does the presence of large amounts of carbonates." The bactericidal action of soap is caused by its colloidal properties, and the greater bactericidal action of any "X"-soap build is the natural sum total of soap and colloidal alkali in "X".

An "X"-soap build of wash wheel strength will completely destroy the non-spore-bearers.

None of the solutions is effective against the spore-bearers.

Elledge and McBride (*American Journal of Public Health*, Concord, vol. 7, pp. 494–498, 1918) also have investigated the bactericidal action of soaps in the power laundry. Concerning this they say:

"Soap solutions at 40° C. may be considered to have real bactericidal value. B. subtilis subjected to the action of soap solution (one part anhydrous soap in 1450 parts of water) was reduced sixty-four per cent. In the case of M. aureus a percentage reduction of 96.1 after an exposure of fifteen minutes and 97.3 after thirty minutes was obtained. With B. coli a percentage reduction of 95.8 in fifteen minutes and 97.9 in thirty minutes was obtained. The washing of clothes with soap thus produces a bactericidal efficiency comparable to that obtained by pasteurization."

As far as skin disinfection is concerned, the sum total of evidence seems to be that it is our most effective agent practicable for everyday use, reducing as it does to a minimum the number of bacteria and the danger of infection, but that its disinfecting action is secondary to its cleansing action. In "Soap as a Vehicle for Medicaments and Disinfectants," (*Chemical Age*, vol. 32, p. 89), Louis W. Bosart sums up his own findings and the majority opinion as to the antiseptic value of soap, in these words:

Soap has marked disinfectant power, but it requires time and a certain concentration of solution to effect germicidal action. Therefore, in the ordinary process of washing the hands or infected skin, its disinfectant power need not be considered.

What soap does is to cleanse thoroughly, removing dust and grease and bacteria, and it softens the skin, thus bringing it into proper condition for treatment with a medicament or disinfectant.

The incorporation of disinfectants or medicaments with soap is not only useless, but since many of the common disinfectants react with the soap, the value of the disinfectant is destroyed and the detergency of the soap is lowered. Even if the disinfectant were of such a nature as to be effective, its action would be nullified on account of the low concentration, the short time of contact, and by the fact that soap is such an excellent cleanser that any disinfectant present would be washed away as thoroughly as the dirt itself would be removed.

As bacteria and spores do not propagate on soap, the danger of infection from using bar soaps is very remote, if not impossible.

Finally, the foregoing may be summarized briefly with the statement that the purest soap is the best disinfectant soap.

CHAPTER IX

OTHER CLEANSERS

Variety and Kinds of Cleansers

The name of these is legion. There are metal polishers of all kinds, dry-cleaning preparations, bleaches, drainpipe cleaners, water softeners, and specialties of many varieties.

Scouring or Polishing Preparations.

Perhaps the most important, judged by the universal need of them, are the various household scouring and polishing compounds for cleaning hard surfaces, such as metals of all kinds, porcelain and tiles, woodwork and floors.

These cleaners, in the form of powders, pastes, and liquids, are in every home, and the tendency is to turn to them for quick action whenever or wherever there is an adherent coating on a surface which is reluctant to leave it with soap and water.

A little thinking, however, should precede this rather mechanical habit of the housewife. Is the coating really one which a non-abrasive detergent will not remove? A scourer or polisher, no matter how fine the abrasive or polishing material, works by friction or abrasion, and seldom does its work without more or less minutely scratching the surface of the article. Is the surface to be cleansed going to be marred by this habitual treatment, so that the article will be less sightly, more inclined to become stained, or less sanitary? If it is necessary to use this type of cleanser, how shall the one be chosen which is adapted to the surface to be cleansed? The average scouring preparation usually claims too wide a range of uses.

Scouring and polishing powders, pastes, or liquids are refinements of the crude mixture of beach sand and soap used for scouring the iron and steel utensils common in former days. As a matter of fact, a few scouring products on the market get their abrasive effects by the incorporation of fine sand from ocean or lake beaches. But just as fine fabrics are in vogue, needing

special care in laundering, so it is the exceptional home which does not have polished metal surfaces—pewter and brass, nickel alloys and aluminum—as well as porcelain tiling and enameled woodwork, all of which make the soap-sand scourer as obsolete as the soft soap of colonial home manufacture.

So while the coarse scouring powder is still in use, and useful, in some cases, the average need in the home at present is for the finer polishing products, and these have been coming into the market in increasing numbers within the last few years. And the problem of choice is created.

Just as in stain removal the rule is to begin with the least harmful of treatments, generally water or soap and water, so the same rule holds good with hard surfaces: a mild detergent first, or a fine polishing substance, leaving the coarser products for the last resort against steel utensils, bottoms of pans, or badly burned-on food. Hot soapy water or solutions of the trisodium phosphate preparations will keep many metallic surfaces bright, particularly nickel and nickel alloys; kerosene does wonders in cleaning porcelain sinks and tiling. But when the use of a scouring or polishing type of cleaner is indicated, the user should have some classification of surfaces on the one hand and types of scourers on the other, in order to fit one properly to the other. For instance, homemakers would group in a special class, requiring the finest grade of polishing material, their jewelry and plate. Both gold and silver are soft, easily scratched metals in the pure form, and only a little less soft when in the common alloys. Pewter, an alloy of tin and lead, contains two soft metals, but is harder than either metal. Nevertheless, its polished surface needs a smooth polisher. Tin, copper, aluminum, nickel, iron and steel rank about in this order from soft to harder. On Moh's scale gold and silver fall between 1 and 3, marble about 3, quartz 7, diamond 10. These figures are not expressive of quantitative differences in hardness, since quartz, such as sand, is ranked about twenty-six times as hard as marble, and volcanic ash, chiefly silica in its nature, is considered to be about eight times as hard as marble.

Tables of hardness may be interpreted as meaning that any metallic substance which stands higher in the table than another will scratch that other. Thus silica and fine sand will scratch gold, silver, pewter, tin, marble, etc. Fine steel wool is used for

polishing aluminum, yet is is harder than aluminum, and if not so finely divided would easily scratch it. If copper wire were used in as fine condition as steel wool, it could not scratch aluminum so much as the latter.

So the question must be considered not only as to the type of material in a cleanser of this nature, but also its degree of fineness and the shape of its particles of abrasive material.

As to fineness and form, laboratories will find the microscope most useful in grading scouring or polishing compounds. Or the material may be sifted through a set of sieves of graded fineness and judged accordingly. Jewelers, for instance, consider a polishing powder which will uniformly pass through a 400-mesh sieve absolutely satisfactory for jewelry and plate. A government specification for a grit soap for scouring and scrubbing calls for material all of which shall pass through a 100-mesh sieve. Many preparations for the household contain material the bulk of which will pass through a 150-mesh or even a 200-mesh sieve, yet will have some particles unable to pass through a 60-mesh sieve. These particles may be comparatively few in number, yet capable of making the entire product unfit for fine surfaces. In the household, a fine sieve or strainer may reveal the degree of fineness and uniformity of some products, and so will the coarser particles which are sometimes found at the bottom of the container. In grading by the sieve method, care must be taken that the abrasive material is dry and free from soap or any product which might cause deceptive lumps to form. A good household test for grittiness is the rubbing test between two glass plates or slides, or even between two finger nails. If the smoothness of tooth powder in this test is observed, a scale of comparison may be built up with other polishing products which will help decide the wisdom of using certain of these products for all of the surfaces often optimistically claimed for them.

Abrasive material, coarse or fine, is frequently silica. Silica is plentiful; it occurs in many forms and in many places; it may be as coarse as sand or ground as fine as silica flour, which will pass through a 400-mesh sieve of bolting silk. It resists solution in acids, except hydrofluoric, and by this may be recognized. According to its various sources as well as the acid test and degree of attrition, it carries marks of identification.

For example, there is the interesting source of silica known as

diatoms or diatomaceous earth. In practically all bodies of water there are algae, minute plants which soon coat stones, logs, etc., with a slimy covering. Diatoms are algae which secrete a silica shield or shell, which they leave behind in dying, to pile up as diatomaceous earth. Even when this material is ground to a considerable fineness, the rounded character of these shells and other characteristics, such as a beaded aspect, can usually be recognized under high magnification. This material is useful in the preparation of the medium fine household polishing products.

Kieselguhr, infusorial earth, and Tripoli are names synonymous with diatomaceous earth, but rottenstone, sometimes called diatomaceous earth, may be of limestone origin.

Lumps of quartz furnish a large part of the silica or silex, as it is called, for abrasive material. The quartz is heated to white heat in a kiln and instantly plunged into cold water, which makes it friable and in condition to be run through crushers and ground to powder. The powder is graded by floating and settling. Amorphous silica, found in Illinois and Maryland, is calcined in a similar manner in the electric furnace, and is capable of being reduced to the extremely fine powder known as silica flour.

When silica so prepared from quartz is found in the medium or coarser abrasive products, it commonly shows sharp, needle-shaped particles under magnification.

Pumice and volcanic ash are found in a large number of products for both coarse and medium scouring purposes. Both are of volcanic origin, and belong chemically to the silica group, being chiefly a mixture of sodium, potassium, and aluminum silicates. Pumice is lava blown to a froth by steam or other gases bursting through it while it is cooling. When cold, this froth turns to stone, and is frequently so porous that it will float. Pumice varies considerably in composition and quality. The best grades are imported from the Lipari Islands and ground in this country. The Rocky Mountain region is a source of both pumice and volcanic ash. Under the microscope pumice is irregular and sometimes granular in character; volcanic ash is ground so as to be mostly in thin flakes resembling broken glass, but particles similar to pumice may be found. Volcanic ash products would have little abrading action were these plate-like particles always to lie flat on the surface to be scoured, but because they have sharp edges and may pile up so that

these edges come into action, their scouring effect may be severe.

In the class of fine polishing substances are chalk, talc (including French chalk and soapstone), and jeweler's rouge.

Precipitated chalk, used for tooth pastes and powders, and sometimes for cleaning silver and jewelry, is a chemically prepared calcium carbonate, which appears under magnification as minute rounded particles. Whiting, or chalk from natural sources, is of course the calcium carbonate shells of foraminifera, which in dying leave their mineral residues to become part of the ooze at sea bottom, and are so vast in extent that they have built up beds of chalk deposits consisting of millions of tons of material, such as in the chalk cliffs of England. Whiting is graded as to fineness, the grades being commercial whiting for the coarsest grade, through Spanish whiting, gilder's whiting, to Paris white. This last and finest grade is sometimes called levigated or floated whiting, and is suitable for silver and other fine surfaces.

Either whiting or precipitated chalk will effervesce with mild acids, due to liberation of carbon dioxide from the carbonate. The carbon dioxide will cloud a drop of lime water suspended in the gas from the point of a glass rod.

Jeweler's rouge is chemically prepared red oxide of iron, and gives a high luster on silver or jewelry. Crocus, also a form of ferric oxide, is used for tin and cutlery. Talc is finely divided magnesium silicate, or rather acid magnesium metasilicate. Both rouge and talc are especially desirable in fine polishing products. The former may be recognized by applying a decided test for iron, and the latter gives a magnesium reaction. According to grade, talc may be much softer than gold or silver, or slightly harder; chalk is about the same in hardness, and ordinary red oxide of iron is harder; rouge, however, being specially prepared, is not so classed.

Soap is a desirable ingredient of these products in that it aids in cleansing as well as acts as a lubricant between the surface and the abrasive. Sodium carbonate is usually a constituent. Typical compositions range from thirty to ninety per cent of abrasive material, zero to fifty per cent of carbonated soda, and one to ten per cent of soap. A silicated-soap-abrasive product on the market for cleaning aluminum does not discolor the

aluminum as much as a soap product which gives up its alkali freely, owing to the buffer action of the silicate.

Metal polishes in cans are liquids with a suspension of polishing material, usually diatomaceous earth or pumice. The liquid may be a mineral oil, with its virtue of removing grease by solution. In this case the product is inflammable. It may be ammonia, also a cleanser and solvent, and not inflammable. The odor affords sufficient recognition of the latter. Or the liquid may be simply a soap solution holding the mineral substance more or less in emulsion form. The reaction of liquid metal polishes should be noted, whether acid or alkaline. Oxalic acid or oxalates give an acid reaction, and are frequently incorporated. They are harmless to copper and brass, but attack nickel or nickel-plated articles.

The electrolytic method of cleaning silver may be mentioned here. It consists of an aluminum pan, or any metallic vessel having an electrical potential apart from that of silver. Tin alone will do, or any pan in which a sheet of aluminum is placed. The silver articles are laid in contact with the metal. The action takes place when boiling water containing an electrolytic substance or carrier of electricity such as bicarbonate of soda, and common salt, is added. An electric current is set up, and hydrogen, released in the interaction of the aluminum and the alkali, passes to the coating of silver sulphide on the silver articles, and reduces it, forming hydrogen sulphide which is released, and leaving the uncoated silver. The odor of hydrogen sulphide is evident in this process. Some objection has been raised to the action of common salt on silver in this operation; if desired, bicarbonate of soda may be used without the salt. The method is useful for heavily embossed or repoussé silver, and as a timesaver in cleaning a quantity of silver. It should not be used for oxidized silver.

Brief reference should be made to a few silver cleaning compounds which are advertised for household use, and which contain a cyanide, usually potassium cyanide. As this salt is a violent poison, there is a risk in keeping such preparations in the house, and in using them. Cases of cyanide poisoning have been ascribed to the use of such preparations in hotels, where some of the product may not have been removed from between tines of forks. The preparations advertise to give a new coat of

silver to worn, plated articles. Look for a poison label on the container.

Furniture and automobile polishes are cleansing as well as finishing preparations, and are similar in composition, although the former are chiefly used on varnished or oiled surfaces and the latter on lacquer, pyroxylin, or baked enamel finishes. In both classes of products can be found oil polishes, wax polishes, and mixed types. A typical oil polisher for furniture contains a mineral oil, a soap for emulsive and cleaning purposes, and often a solvent such as wood or amyl alcohol or their esters, kerosene or turpentine. Triethanolamine, which is said to have no injurious effect on lacquer finishes, has been introduced as an emulsifier of waxes and hydrocarbon oils. The emulsion remains stable when water is added so that the products are usable as liquid polishes, sprays and cleaning compounds. Some of the commercial polishes are inexpensive to prepare, and have only the temporary effect of cleansing and overlaying the surface with a thin film which may collect dust. The constant use of the product may increase the thickness of this film until the mixture of hardened oil and dust has to be removed by strenuous methods. The cleansing compound which they may contain, such as wood alcohol, may be detrimental to the finish of furniture unless its action is buffered by other ingredients. Wax polishes in liquid or paste form have a more lasting effect on floors and furniture, and a somewhat preservative action on the pores of the wood. Naturally no abrasive material should be in a furniture polish, and if found at all in an automobile soap, it should be of a fineness suitable for silver.

Circular No. 70 of the Bureau of Standards, Washington, D. C., entitled *Materials for the Household*, gives recipes for the preparation of wood polishes, of which the following is one:

Turpentine	One pint
Beeswax	Four ounces
Aqua ammonia	Three ounces
Water	One pint

Mix the beeswax and turpentine, heating them by placing the container in a kettle of hot water (turpentine is inflammable) until the beeswax dissolves. Remove from the hot water, add ammonia and water, and stir vigorously until creamy.

Commercial wax polishes are made in a similar way, the desired combination of waxes, perhaps paraffin, ceresin, and car-

nauba as well as beeswax, being melted in a steam-jacketed kettle and the solvent, either turpentine or a mixture containing turpentine, stirred in slowly. The difference between a liquid and a solid floor wax is in the amount of wax content. Paste wax should as a rule be used for a heavy coating on new floors, after which liquid wax will keep the floor built up. Linoleum may not need paste wax at all, since it absorbs less than wood and will be sufficiently coated with one or two applications of liquid wax from time to time.

A solid or paste wax should contain at least twenty per cent wax or a mixture of waxes, the melting point of which should not be below about 168° F. If the wax is too hard it gives a brilliant polish which may show scratches; if too soft, a dull effect. A liquid wax should contain at least twelve per cent wax, and turpentine or a mixture of turpentine with other organic solvents of the wax. These solvents volatilize from the wax as it is used, but they constitute a fire hazard, and for that reason those with a low flash point, such as petroleum ether, should not be incorporated.

On the whole, the newer scourers and polishers on the market tend very much toward finely divided abrasive material, even when recommended for general purposes. Fine pumice, diatoms, and whiting are more frequently found than ground flint, coarse marble flour, and silex. So the newer needs of the house are being met, if the consumer will be intelligent in purchase and use. The variations in composition which put so many new products on the market are found in the ingredients other than the abrasive, as a rule. Here are some sample compositions:

A paste for glazed tiles, paint and enamel contains carbonated soda, silicated soda, pumice, soap, water, and glycerol. The latter ingredient keeps the mixture from drying.

One mixture for scouring porcelain contains sodium bisulphate and talc.

Another quite different material includes coarsely ground wood pulp, salt, sodium sulphate and sodium bisulphate, and traces of silica.

A cleanser for metals, recommended especially for aluminum, consists of soap, an oxalate, and a coarse silica abrasive.

Another, advertised to clean silks, velvets, laces, and jewelry, is composed essentially of soap, carbonated soda, borax, bluing,

and fuller's earth. Fuller's earth is an absorbent and adsorbent clay often used to remove grease from delicate or non-washable material, for instance fine laces, collars of dresses or coats, and furs.

Rust removers often add to the abrasive a small amount of oxalic acid and a fluoride, e.g. ammonium fluoride. This type of remover is used especially for stone or metal surfaces, but fluorides are also used to remove rust spots from fabrics.

A study of silver polishing preparations shows less range in composition. A fine grade of whiting is most frequently found; sometimes jeweler's rouge; less often a fine rottenstone. If the product is a paste, soap is a usual ingredient, and glycerol. Hydrocarbon oils and ammonia may be additions. An essential oil such as oil of wintergreen or sassafras is incorporated for prevention of rancidity as much as for agreeable odor. A liquid polish differs essentially from a paste only in the amount of moisture it carries, and is less economical to purchase. A few preparations on the market vary from the usual type by introducing sodium thiosulphate, which is a solvent for the tarnish on silver; or potassium or silver cyanide for replating effect.

A satisfactory silver polish may be made at home by buying as fine a grade of whiting as possible, and washing it through fine cheesecloth into water. The whiting which goes through may be used for silver; the residue for less delicate surfaces. The fine whiting is mixed with a soap jelly until a paste is formed, and the addition of a little glycerol will keep the paste from drying out and becoming friable. More water may be added at any time.

Soap Powders

"Soap powders" are not soaps entirely, nor are they abrasive products. They are ordinarily composed of less than twenty per cent of soap, the balance, excluding moisture, being soda ash, silicated soda, trisodium phosphate, ammonium chloride or carbonate—any of these or other substances. Their function is to soften hard water and to act as a general assistant in cleaning rather than as the chief detergent in laundry work. Estimating the actual cost of the contents, it is clear that the purchaser pays from three to five times what the essential products bought in bulk would cost, for the sake of the convenience of the form. But this is not an unfavorable criticism, for many overhead costs go into the pricing of any product. These soap powders and

trisodium phosphate preparations are discussed more fully in Chapter X.

A few compounds are on the market which have a specific use in cleaning and disinfecting toilet bowls and drain pipes. They are strong chemicals as a rule, and must be used only for the purpose recommended, and with regard to the directions. Several for toilet bowls are strongly acid, containing what is known as niter cake, or commercial acid sodium sulphate. Coloring matter and some kind of an essential oil or a disinfectant are often added. Compounds for cleaning drain pipes and traps are sometimes dry preparations of caustic soda, together with particles of a metallic substance such as aluminum. The latter releases hydrogen from the solution which forms when the dry caustic soda meets the water in the drain pipe; the active effervescence of this hydrogen, coupled with the heat of the solution of caustic soda, results in stirring up the contents of the pipe or trap, melting the fats, and causing chemical combination of these with the caustic lye to form soluble soaps.

Dry-Cleaning Preparations

These constitute a numerous and important class of cleaning compounds. Usually they are found in liquid form, and contain one or more of the standard organic solvents for fats, such as chloroform, carbon tetrachloride, kerosene, gasoline or cleaning naphtha, benzol, and acetone.

An evaluation of these compounds has several practical aspects. How much do they cost in comparison with the same amount of certain well known cleaning fluids such as carbon tetrachloride, purchased in bulk? Five pounds of technical carbon tetrachloride may be purchased at some chemical supply houses for a little over one dollar. Five pounds of this commodity approximate 1.4 liters, or about three pints. Counting the average retail cost of one quart, or about one liter, at one dollar, a comparative study was made of the cost of twenty-three dry-cleaning preparations bought in small bottles. Based on the cost of the contents, two preparations were priced at the rate of about $1 per liter; three at a little less than $2; seven between $2 and $2.50; seven between $2.50 and $3; one at $3.72; one at $4.38.

These price comparisons are subject to variation, as prices will vary with different merchandisers and in different years. But

they serve to call attention to the fact that it is usually cheaper to purchase in bulk, provided quality and performance are equal to the proprietary article.

It might be thought that the more expensive of these preparations would have shown superior merit, but practical tests on various materials did not bear this out. In fact, the three most expensive, and the three least expensive, of these cleaners dropped to the lower half of the list when rated for performance. One of the most efficient was practically unmixed carbon tetrachloride, but in the small bottle it cost more than twice what this cleaner costs in bulk.

One most important thing in respect to these cleaners, which the user must notice, is a warning against fire which the label may carry. In that case the cleaner contains an excess of gasoline or cleaning naphtha, benzol, acetone, or similar inflammable liquids. These are all dangerous if an open flame is near, and gasoline or cleaning naphtha has been known to ignite from a spark of static electricity produced by rubbing wool or silk. Chloroform and carbon tetrachloride, on the other hand, are fire extinguishers. Chloroform is less used in these products, being more expensive and subject to chemical change which makes it poisonous to breathe. No one of these compounds is wholesomely breathed for long periods, and dry-cleaning should be done in a current of fresh air or out-of-doors.

A few of these compounds, notably those which contain acetone, have a weakening and dissolving effect on the cellulose acetate type of synthetic fibers, but not on the other types. Carbon tetrachloride does not have this effect.

Some dry-cleaning preparations are found which contain a naphtha-soluble soap to be used in combination with the grease solvent. This is a good type of cleaner. In Chapter II was found a discussion of the penetrating power of grease solvents in regard to the fiber cell, as compared with a soap cleanser. Commercial dry cleaners know the virtue of soap combinations, and use for their naphtha-soluble soaps a type of soap containing free fatty acids. In fact, soap and water is used in preference to dry-cleaning solvents in dry-cleaning establishments, much more than the public is aware, for practically all fabrics are washable with the right soap and the right method, and real cleanliness results.

Most of the commercial dry-cleaning preparations lay adver-

tising stress on leaving no ring; many claim to remove other than grease stains, such as ink, coffee, and fruit. As to the former claim, the amount of ring formation depends upon the character of the fabric, the surface finish, the weighting or dressing it contains, the dirt or soil in the material, and the method of applying the cleaner, quite as much as upon the peculiar virtue of the solvent itself. Yet the statement leads to the conclusion that the ring will not show in any case. As to the removal of other stains, no cleaner was completely effective, except where the stain had an element of grease in it, as in paint.

The consumer should evaluate these cleaners carefully in comparison with the bulk type of grease solvent, and use the kind which satisfies her as to performance and economy. In many cases, dry-cleaning should not be attempted at home, but should be done by an expert.

Chlorine Bleaches

Recently we have all added to our shelf of cleansers one or more of the preparations in liquid form which are the equivalent of the solution known as Javelle water. If the consumer will read the label on these bottles to note the available chlorine, or the phenol coefficient, she may have more or less of a guide to the bleaching strength of the article, and by comparison, its right pricing. There are variations in value, as well as in price. One which is too highly priced is nearly all water, with about five per cent carbonated soda and only a very small amount of available chlorine. Others are effectively prepared and have active bleaching properties. They should be used cautiously in as dilute solution as possible, at low temperatures, unless disinfection is also a requirement.

CHAPTER X

TESTS AND EVALUATIONS OF DETERGENTS

Analysis by Types

For a number of years the Department of Household Chemistry in Teachers College, Columbia University, has been interested in comparisons and evaluations of detergents. The writer, taking an active part in this work, has studied many of the old and new forms of cleansers with regard to their composition, detergent efficiency, and effect on the strength, color, or general character of the fabrics tested.

This chapter gives a general survey of some of these evaluations, but with regard to specific products the results are not for publication, obviously, nor for emphasis in teaching such material. It is by types, as much as possible, with some variation within the types, that the student or consumer should estimate a product, and fit its use to different laundry purposes.

The tests reported are therefore indicative of the type of detergent, and have to do with analysis, measurement of surface tension, hydrogen ion concentration, penetration of dirt into fiber cells and its removal by different types of cleansers, and other physical and chemical comparisons which may be translated into a basis of knowledge for purchase and use.

For the analysis of soaps and similar products, recognized standard methods were followed, such as are given in Griffin's *Technical Methods of Analysis* and Allen's *Commercial Organic Analysis*, Vol. II. In order to give the results the practical value of easily understandable terms, the following reports tell the approximate amount of moisture or volatile matter, soap, and other principal ingredients in the product; whether it is strong or mild, and where it belongs in the detergency problem.

Bar Soaps

Bar soaps, which are the oldest members of the soap family, still hold their place in the household, and are particularly useful

whenever soap has to be rubbed directly on a soiled surface. Laundry bar soaps are of two types, the white and the yellow; the difference between these has been pointed out in Chapter IV. On analysis, both are found to conform to the general composition of one part water or volatile matter, one part soap, and one part rosin soap or sodium silicate, depending upon the yellow or white type. Frequently the moisture is less and the soap more than these rough proportions. In a comparison of several soaps, a popular yellow laundry bar gave an average analysis of twenty-eight per cent volatile matter, nearly seventy per cent total soap, or a combination of fatty acid and rosin soaps, and small amounts of free alkali, carbonated soda, and sodium chloride. Another rosin soap with a similar composition, contained an addition of a small amount of naphtha or hydrocarbon oil. A third sample ran true to this general composition, with the addition of about one per cent of borax. Two typical white laundry bars, one containing naphtha, showed slightly over thirty per cent volatile matter, and approximately twenty-five per cent sodium silicate. The free alkali in bar soaps sometimes exceeds the safe or desirable amount, which is recognized as being not more than one-half per cent. The pH values of the stronger bar soaps are about 11. Such soaps, and indeed bar soaps in general, excluding the semi-toilet or bath variety, are designed for the washing of the coarser fabrics or for rough cleaning, while the flaked soaps which follow are uniformly for fine fabrics and delicate colors.

Flaked Soaps

With few exceptions, the well known members of this flake-soap class are mild soaps, that is, they contain little or no free alkali. Nationally advertised brands need no particular recommendation of one or disparagement of another. As a rule, the moisture content is very low, averaging from two to five per cent. This indicates a pure soap, for the presence of carbonated soda as washing soda, or other hydrated alkaline salts would considerably increase the amount of volatile matter. It follows that these soaps are concentrated, more so than almost any other form, and are therefore economical if used as concentrated soaps. Practically all the remaining ninety-odd per cent is well made, mild soap, containing such small amounts of other substances that the report is negligible. Since in soft water nothing cleanses better

than a pure, concentrated soap, these products rank high in efficiency if not wastefully used. They are suited to cool water laundering because of the generally low titer of their fatty bases.

The hydrogen ion concentration of the standard brands is low, seldom rising above pH 10. Three standard brands were given a series of readings in the potentiometer, with only slight variations from pH 9.8 to pH 10. These samples were bought at different times and in different cities, and the uniformity of the results showed the care taken to have every batch of soap run true to specifications.

Other pH readings were made with the LaMotte roulette instrument, and checked by the Hellige apparatus. A reading of pH 10 or under was considered to show a mild soap for general fine laundry work, although a few special soaps for shampooing or fine toilet uses may approach more nearly the neutral pH 7. But no soap made from an alkaline mineral base is neutral in water solution, in which pH readings are made. A pH from 10 to 10.5 or 10.6 appears to be a fair range for the general home laundry, and above this come the strong soaps which are sometimes soap-water-softener combinations and are useful for the heavier laundry work at times.

Floating Soaps

For semi-toilet use floating soaps are, in the case of several well known brands, very similar to flake soaps in general composition, except that since in the bar form there is more moisture, there is a corresponding drop in the percentage of soap. Fifteen to twenty-five per cent of moisture may be found in such soaps, depending partly upon the fresh or dry condition of the soap. It is economical to allow all bar soaps to dry for some time if they seem fresh, so that they will not waste away in use. In laundry performance these soaps will usually have the effect of the flake soaps mentioned above, except that as the concentration of soap is less, more of the product is required for a given amount of work. The flaked type should be chosen for laundering when possible, since it is a timesaver in making the soap solution.

Soap Chips

There are many nationally known brands of soap chips. They are popular because they are particularly suitable for the washing

machine. But due partly to variations in the degree of hardness of waters in different regions, with sundry additions made to these products for water softening and other purposes there is found a wider range of composition than in the flake variety. The moisture content may vary from five to fifteen per cent; therefore these products stand between flakes and bars in this respect.

Two or three brands of soap chips were found to be close equivalents of mild flake soaps in composition. One of these, put out by a leading manufacturing company, was about equal in rank with any flake soap in its adaptability to the laundering of wool, silk, or synthetic material. It contained ninety-four per cent of detergent material, mostly soap with a small amount or trace of rosin soap, and a very little carbonated soda. The alkalinity of this product was found to be about pH 10.

Another chip product, of fairly mild quality, contained about nine per cent moisture, seventy-four per cent soap, and about thirteen per cent borax. The borax, in spite of its slight water-softening action, is not the equivalent in its detergent value of an equal amount of pure soap in soft water. Nevertheless, the alkalinity of borax is not high enough to harm most fabrics, and some of these borax products are well made and good.

Varieties of flake or chip soaps which contain a blue dye for the purpose of bluing clothing in the wash water are on the market but are not yet numerous. Among a few kinds evaluated one or two are outstanding in quality, and where they are intended to supplement the regular laundry soap they add the value of a high-grade, concentrated soap to the washing operation. The blue color, a dye in character, does not objectionably dye the clothing, since it is not being applied under the conditions for the permanent fixing of the color. The prejudice which has existed against putting in the bluing at the time of washing the clothes is disappearing, now that the use of the mechanical washer ensures clean clothing, which may not always have been so certain if with careless methods of hand laundering the bluing covered a certain amount of grime. It is often time-saving to combine bluing and washing.

Some chip soaps of standard makes are silicated. One representative product contains about twenty-two per cent volatile matter, sixty-four per cent soap, four per cent carbonated soda, and eight per cent sodium silicate. If soap chips have a brittle

rather than a velvety feel, this may be due to silicate or to excess carbonated soda, usually to silicate. Carbonated soda, as most school children know sooner or later, may be tested simply by pouring a mild acid, such as vinegar, over the product and noting the effervescence of carbon dioxide set free from the carbonate. As has been said, sodium silicate in moderate amounts is not undesirable in a product for general laundry purposes.

Taken as a class, soap chips represent an economical form of detergent of generally good quality. They are less expensive than the flake form, and go into quick solution in the washing machine or tub.

Grains, Beads, and Powders

New products which appear are more and more in the form of grains, beads, and powders. The tendency to-day is to subdivide laundry products ever more finely, in order to save a few minutes or seconds in dissolving them. One rather serious disadvantage in the use of such finely divided products is the ease with which they fly into the air while pouring from the package, and irritate the nasal passages. Another is the possibility of waste, since they pour out so rapidly. But the advantage of quick solution and perhaps quicker rinsing cannot be denied.

A well known bead soap for general laundry use analyses about five per cent volatile matter, sixty-three per cent soap, of which about two per cent is rosin soap, sixteen per cent carbonated soda, and fifteen per cent silicated soda. The alkalinity of this product is about pH 10.6. Its composition indicates that it will be more efficient in water of some hardness than in soft water, since approximately thirty per cent of its composition represents material which has water-softening action, and a buffer action in restraining soap hydrolysis.

Powdered soaps and soap grains frequently approach soap powders in composition, because the form allows a considerable admixture of carbonated soda or other crystalline alkaline material to be incorporated. Therefore there is considerable variation in composition, and it is in this field that the consumer will find it most difficult to exercise judgment. One granular product has its detergent material about equally divided between soap and carbonated soda. The percentage of volatile matter is high,

because so much is held by the carbonated soda as water of crystallization. According to its efficiency this product is fairly priced, but its best field of action is naturally in hard water sections. Its pH value is about 10.8, which is fairly high, and much of its detergent action is chemical. Unless they meet her laundry requirements, no consumer needs to use this or any product containing a high percentage of carbonated soda, if she will note the decided effervescence which vinegar will give with such products.

A few products in grain or powdered form are advertised to have a bleaching action. Sodium perborate has been found to be the bleaching agent in one or two cases. Oxygen is given off from its solution. The composition of one such product is about thirty-five per cent soap, thirty per cent carbonated soda, and ten per cent sodium perborate, the balance being volatile matter and sodium silicate. The alkalinity approaches pH 11. Another, of better grade, contains about eight per cent volatile matter, seventy per cent soap, and the remainder carbonated soda and sodium perborate. An evaluation of the effect of these products on fabrics, in comparison with non-bleaching soaps, is found in the section on fabric testing which follows later in this chapter. For occasional use, always remembering the chemical effect of bleaching, these products are convenient.

The idea of starch in some form as a filler of soap products is revived from time to time, although there is little evidence that such products ever achieve much popularity. Two have appeared recently. One such product contains about eighteen per cent volatile matter, thirty-seven per cent carbonated soda, five per cent corn meal or corn flour, and about forty per cent soap. Another increases the corn meal to about seventeen per cent and the soap to nearly fifty per cent, with a lessening of the amount of carbonated soda. Sometimes the starchy bulk of cottonseed meal has been incorporated. The claim which some of these products make of superior mildness for the washing of silks and woolens is not borne out by test, nor by their composition, since the amount of carbonated soda in the products analysed was too high. Probably this is necessary in order to check rancidity. Just how much value the starchy material has as a lubricant and a buffer between the free alkali and the fabric, is uncertain. Hot water would defeat the purpose of the starch in this respect, as it

would cook starch and dirt together in the interstices of the fabric. Nor is it a good plan to use such a soap for washing underwear, for starch is a poor rinser, and will collect in the pores of the garment and clog them. If a solution of such a soap is acidified, the starch test may be made with iodine, and the microscope will identify the source.

More extravagant claims are made for new products in the powder or grain form than for any other type, it seems. One ten-ounce package was priced in New York City markets at one dollar, the consumer being expected to believe, of course, in miraculous powers commensurate with the price. The actual contents were worth about five cents. Analysis showed the essential constituents to be about forty per cent soap and about as much carbonated soda. This product faded from the city market, but a similar one appeared later in the South, where it was sold by house to house salesmen under a different name but at the same price. The salesmen are quoted as saying that "it will clean silk dresses or anything."

Soap powders, intended to be used as water softeners in conjunction with soap, or for special cleaning, contain on an average eight to seventeen per cent volatile matter, fifteen to twenty-five per cent soap (fifty per cent in one product sold in bulk), with the remainder chiefly carbonated soda.

Newer forms of these water softeners may be almost entirely trisodium phosphate, or a mixture of this product with other ingredients. A product in which there is rather less of the trisodium phosphate than is usual in such mixtures contains thirty-seven per cent volatile matter, thirty-six per cent carbonated soda, thirteen per cent borax, and fourteen per cent trisodium phosphate. Another well advertised product has the same ingredients in different proportions, with more of the phosphate. Another adds a slight amount of soap to these substances. Another contains trisodium phosphate, carbonated and silicated soda, and ammonium chloride. Still another adds bluing. One in tablet form, advertised for all kinds of cleansing, from shampooing to washing dirty floors, is chiefly trisodium phosphate, bound in tablets by cornstarch or corn flour. The latter takes up water and causes the tablet to disintegrate when used. It is an alkaline product, with a pH of 11, not at all suited to uses demanding a mild detergent. It must be remembered that these are crystalline

products, which have little or no physical action similar to that of a colloid in cleansing; therefore they cleanse by chemical action, and their alkalinity, although not so high as the caustic type, nevertheless is sufficient to be undesirable for silk and wool at least.

Since variations of the trisodium phosphate preparations are on the market in great numbers, their values and uses should be understood. Their most outstanding excellence is in softening water, and in washing glassware, tiling and porcelain, dairy equipment, and in other instances where the lingering film of soapsuds is not desirable. In some cases package directions are sensibly restrained, and emphasize the auxiliary character of the product with soap in washing. The lack of suds is a means of recognizing trisodium phosphate cleaners.

Liquid Soaps and Soap Jellies

Liquid soaps and soap jellies are of questionably high price for laundry use because of the extreme moisture content in most cases, and the cost of the tin or glass container. Considering some of these products, exclusive of the liquid soaps sold in bulk and desirable in public washrooms, we found that one product contained ninety per cent water, the detergent materials being a small amount of soap, some carbonated soda, and a chlorine bleach. The cost was twenty-five cents for twenty-eight ounces. Another cost twenty-five cents per pint, and contained ninety-six per cent moisture and three per cent soap, with a trace of borax. The same product could be duplicated in the household for about two cents.

But in this class of liquids or jellies there are some products of more intricate composition and greater value. They often contain an essential oil, which gives antiseptic value and an agreeable odor. Some of the pine or resin oils are frequently found. The soap may be made with a potash base, and it may be a linseed oil soap. The alkalinity is often carefully regulated, so that the products are justly advertised as suited to shampooing, to washing silks and woolens, or to cleaning linoleum. Cost and use should be carefully considered before the purchase is made. Frequently a soap jelly made at home from a mild soap will do as well or better for washing rugs and carpets, uses often dominant in the advertising of these specialties.

Physical Tests

Surface Tension Measurements

The surface tension measurements were made with several different types of soaps: Pure, mild flake and chip types; a carbonated granular soap; a carbonated silicated bead soap; a borax chip soap; a rosin bar soap; two silicated bar soaps, one containing naphtha; two trisodium phosphate preparations, and anhydrous sodium carbonate. Three temperatures were used, namely, 20°, 40°, and 80° C. Increasing strengths of solution were compared, namely, 0.025, 0.05, 0.15, and 0.25 per cents. The instrument used was the du Noüy surface tensiometer.

The object of the tests was to determine any marked differences in the surface tensions of equivalent solutions of different types of soaps, in varying strengths of solution and at increasing temperatures. The result may be considered to be one check on the detergent power of the product, since by its ability to spread through its low surface tension, a soap solution exercises an important detergent function.

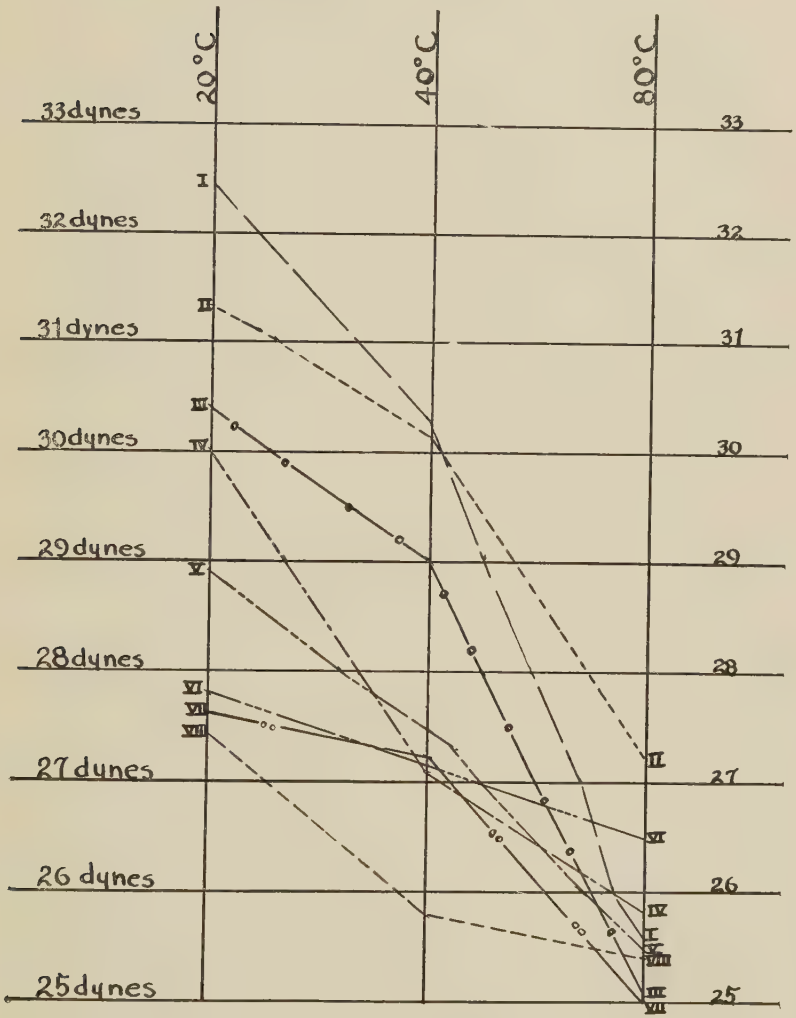
Several conclusions were evident as a result of these tests:

1. With increase in strength of solution there was a decided drop in surface tension, from three to eight dynes. There were no exceptions to this finding. But it does not necessarily follow from this that the stronger the soap solution, the more efficient it is as a detergent, because there comes a physical limit to the amount of suds necessary or desirable. When the more greasy soiled places are rubbed directly with soap, however, the lower surface tension of the concentrated solution aids in emulsifying the grease. Experience has established that a 0.25 per cent solution is a maximum average strength for efficient home laundering.

This strength of solution has been selected to show in the accompanying graphs the comparative surface tensions found.

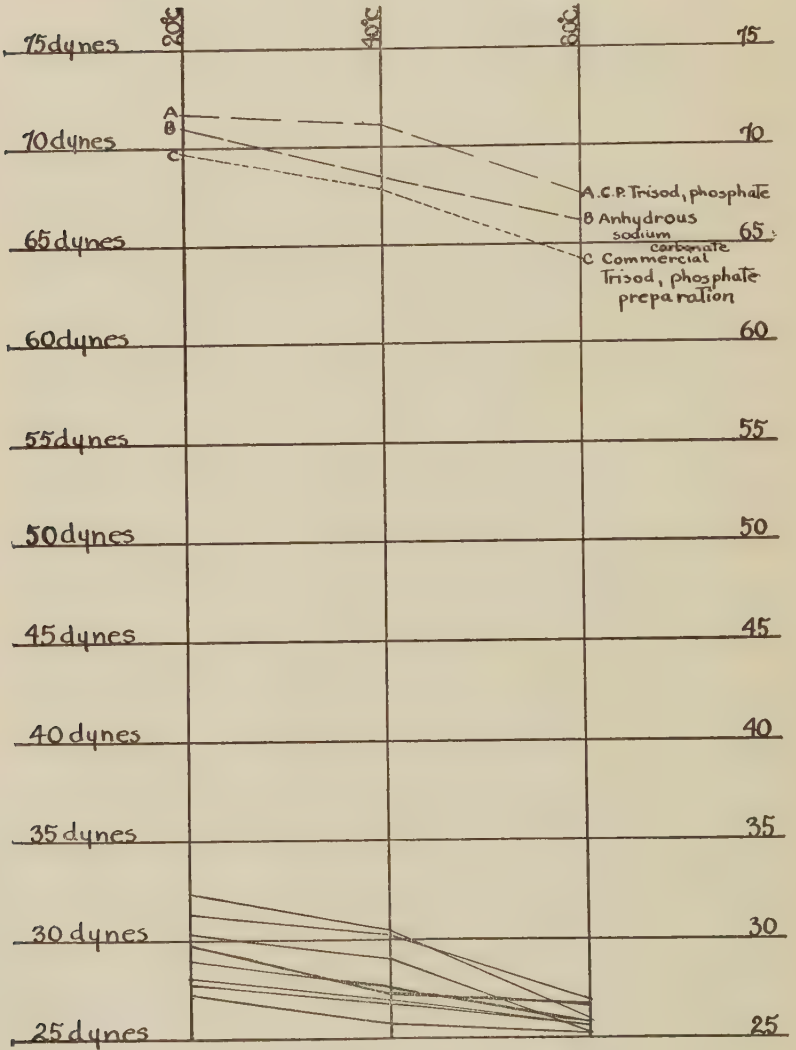
2. There was also a decided drop in surface tension with increase in temperature, which is shown in the graphs. This is in accordance with the rule that the surface tension of liquids diminishes as they approach the gaseous condition. The drop in temperature between 20° C. and 40° C. is so decided that the latter temperature is clearly more efficient than very cold water for the laundering of fabrics which are counted to need a moderate temperature.

COMPARATIVE SURFACE TENSIONS



I. A pure flake soap
II. A naphtha-rosin soap
III. A pure flake soap
IV. A carbonated soap
V. A carbonated-silicated soap
VI. A rosin soap
VII. A borax soap
VIII. A silicated soap

COMPARATIVE SURFACE TENSIONS



Above: Non-soap products
Below: Soap

3. The tests also showed that some soaps are more efficient in cold water than others, as far as surface tension goes, but that the grouping becomes closer at blood heat (about 40° C.) and at 80° C.

4. Soap products are far superior to trisodium phosphate or carbonated soda alone, in low surface tension, with what that connotes in cleansing power.

The low surface tension of all soap products is a very important factor in cleansing, but one soap product should not be judged superior to another solely because its surface tension may be lower by a few dynes. Other properties may negate this advantage for a particular purpose, and the final rating of a soap should take into account as many qualities as possible.

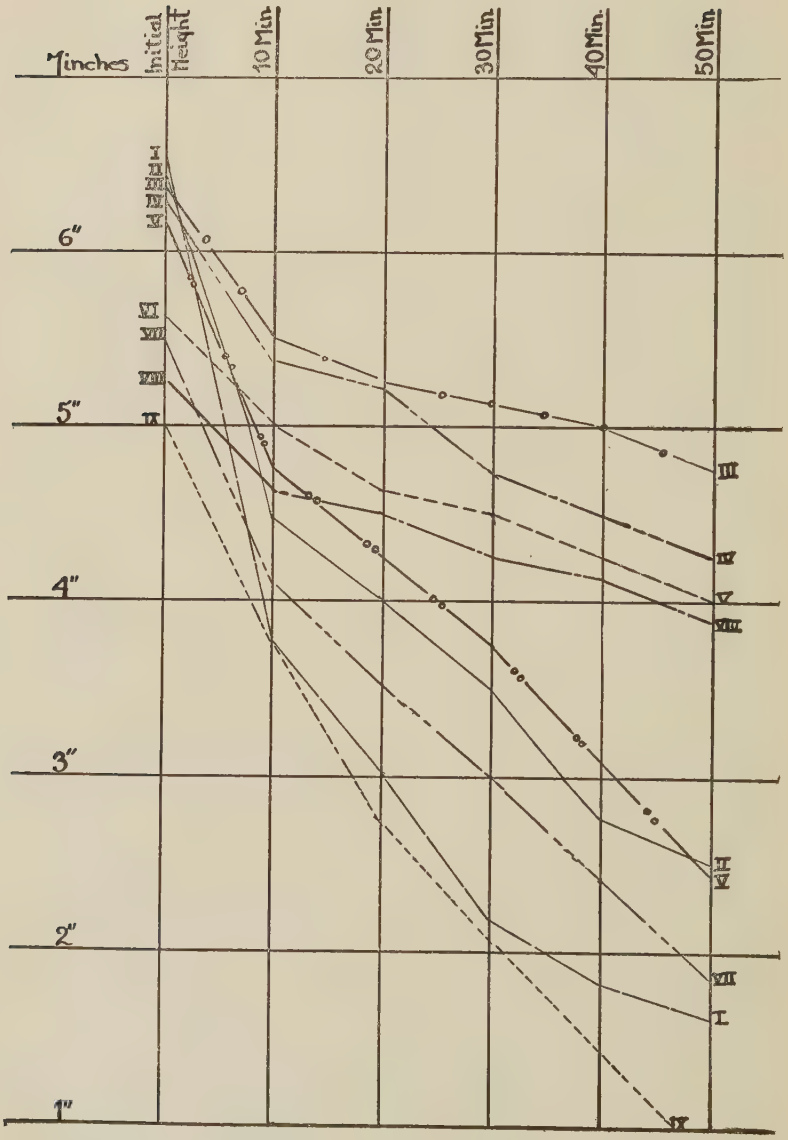
In the first of the following graphs, the comparative surface tensions of different type soaps is emphasized; in the second graph, the comparison is made between cleansers of the soap type and the non-soap products.

Sudsing Power

The efficiency of a soap is in a measure related to its sudsing power; therefore a test of the amount and character of the suds produced by a soap is a part of its rating. In the suds tests here reported, a number of typical soaps were dissolved in 0.25 per cent solutions, and at 120° F. were beaten with an electric stirrer under the same conditions of speed, time, amount of solution, and size and shape of container. The initial height of the suds was measured as soon as the motion ceased, and succeeding heights at ten-minute intervals.

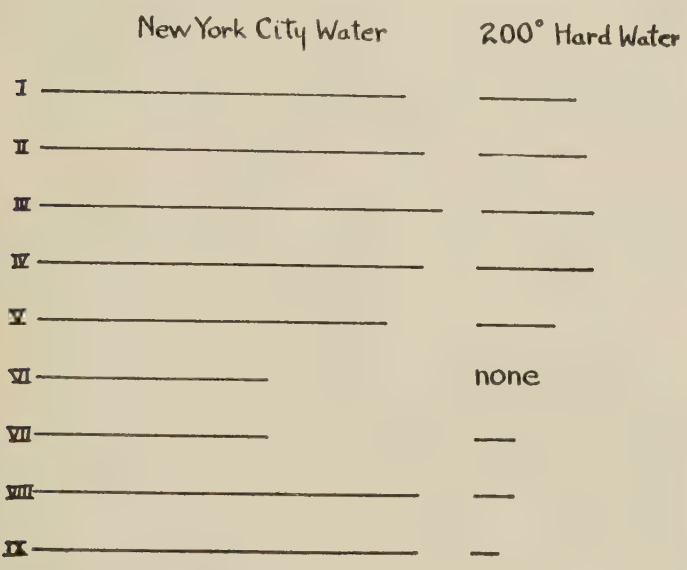
The graph which follows shows the initial height of the suds in inches, and the heights at ten-minute intervals up to fifty minutes. The four soaps which not only had a high initial suds but retained a much greater amount at the end of fifty minutes were all mild soaps, three of them of the flake variety and one a mild chip soap with no carbonate. From one to two inches less in height of suds at the end of fifty minutes were found a borax chip soap, a carbonated granular soap, and a chip soap containing some silicate; then came a bar silicated soap, a soap containing corn meal, a rosin naphtha soap, a rosin bar soap, and last of all, with no suds remaining, a bleach soap containing sodium perborate and some carbonated soda.

HEIGHT AND PERMANENCE OF SUDS



I. A naphtha-rosin soap
II. A carbonated soap
III. A mild flake soap
IV. A mild chip soap
V. A borax soap
VI. A mild flake soap
VII. A soap containing corn meal
VIII. A mild flake soap
IX. A bleach soap

A second graph shows comparisons in suds formation in hard water.



I–V. Soaps with little or no builder
VI. A naphtha soap
VII. A borax soap
VIII. A silicated soap
IX. A carbonated soap
———=1″ height of suds

Emulsification Tests

The emulsification tests were carried out by introducing in long-necked bottles, under the same temperature conditions, equivalent solutions of different soaps and, as determined by previous trial, enough vegetable oil to leave a small residue unemulsified at the end of the test. After warming and vigorous shaking under exact conditions, the mixture of soap and oil was placed in a water bath at 140° F. for fifteen minutes, to allow unemulsified oil to rise in the narrow neck of the bottle, where measurement could be made. Checks of these tests showed that a division could be made between the depths of the series of unemulsified oils, one part showing one-half inch or less, the other division more than one-half inch in depth. This was taken as a dividing line for grouping the soap types. Those soaps which showed by this test the greatest emulsifying power were three mild flake soaps, a

mild chip soap, a flake soap containing bluing, a mild bar soap containing about eighteen per cent moisture and a negligible amount of builder. In the second class were a highly carbonated granular soap, two naphtha soaps (one containing sodium silicate and the other rosin), and a washing powder. The indications of this test are that those soaps which contain the greatest amount of actual soap can usually be depended upon to be the best emulsifiers.

Washing Tests

Washing tests of many kinds, on many sorts of fabrics, have been carried on for several years. Two aims have been kept in mind: to compare different types of soaps, first, as to efficiency, and second, as to effect on fabric strength.

In one test a comparison was made between three mild soaps, all flake products, as to their effect on the strength of silk, wool, and fine cotton material. Initial and final strength tests were made on the Scott Cloth Tester. The tests included soaking at different temperatures, namely, 100°, 120°, and 180° F., for sixteen hours; washing at these temperatures; and boiling for one hour, using a reflux condenser to keep the soap solutions as nearly as possible at constant strength. Solutions of 0.25, 0.50, and 1.0 per cent strength were used. The boiling test was not, of course, a comparison in detergency, but a means of judging the effect of any increased alkalinity in one product over another. In addition to these tests, other comparisons between these three soaps were made, including sudsing, hydrogen ion concentration, surface tension, and analyses.

The results of these tests show no very decided advantage in the use of any one of these three soaps, when all are used in tepid water with correct laundering methods. But when strenuous tests with high temperatures are applied, as shown by the effect on wool in the boiling test, the flake soap which contained coconut oil as its principal fatty constituent showed its slightly lower hydrogen ion concentration, and milder alkalinity. Wool boiled in this soap solution showed a better color and a slightly higher tensile strength than that resulting from the other two boiling tests. Probably the effect is due to the lower degree of dissociation of a coconut oil soap as compared with the soaps of higher fatty acids. This test is mentioned because it may be possible by

the use of exact methods, even in the household, to make a qualitative comparison of mild soaps, and with no difficulty it shows the difference between a mild and a harsh soap.

A second series of tests, upon wool flannel alone, used only the correct method of laundering wool, with eight different soap types as the variables. Ten washings were given pieces of the material of equal size, using solutions of equivalent strength based on the dry soap, at the same initial temperature (100° F.), and in a machine which standardized speed and eliminated handling. Rinsings were likewise standardized. Color, shrinkage, and tensile strength were the comparisons determined. The ranking of the samples as to shrinkage, in the order of least to most, was (1) that washed with a mild flake soap; (2) a mild chip soap slightly more alkaline than the above; (3) equal in shrinkage, a borax soap, a bleaching soap, and a white naphtha; (4) a yellow bar soap; (5) a strongly carbonated product; (6) a trisodium phosphate preparation. The whiteness of the flannel varied in about the same order, the samples most deeply yellow being those washed ten times in the carbonated and trisodium phosphate products. Tensile strength tests were not so definitely determined, owing to the effect of shrinkages, those samples which shrink most ordinarily having increased strength due to the drawing up of the fabric, unless the effect of the alkali nullifies this; but the least loss of strength considering surface area was observed in the mild soap test, and the greatest in the sample washed with the bleaching soap.

The effect of a bleach on the strength of any fabric, whether that bleach is a natural or a chemical one, has been emphasized. We quote from "The Influence of Laundering on Cotton Fabrics, Especially with Washing Agents Containing Sodium Perborate," by P. E. Raaschou and V. Ahrend Larsen, as described in *Industrial and Engineering Chemistry*, vol. 20, No. 9, pp. 916 *et seq.* The investigators state in their summary that:

> The addition of a small quantity of perborate (0.01 per cent of the lye) to these solutions (1 per cent of soda, 0.5 per cent of sodium hydroxide, 1 per cent of water glass, or 1 per cent of soap in hard water) increases the weakening, which in certain cases, however, is slight in comparison with the weakening influence of the pure laundering agent. The addition of increasing quantities of perborate (0.01 to 0.15 per cent of the washing lye) to the standard lye causes a pronounced decrease in strength. Special boiling of the fabric causes an additional weakening, when the boiling is done with the standard lye plus

0.05 per cent of perborate. On boiling with distilled water (containing a trace of copper) an especially pronounced weakening is found when the standard lye plus 0.05 per cent of perborate is used. A comparison of breaking strength tests with tests on the dissociation of the perborate during the boilings shows that boiling with a lye retarding the perborate dissociation results in a low degree of perborate weakening, and vice versa.

A series of tests with a similar purpose were carried out in the Household Chemistry laboratory of Teachers College. In these tests New York City water, which is soft, was used. The test detergents were three laundry products: a perborate soap, a mildly silicated chip soap, and a quite highly carbonated granular soap. Three fabrics were used: a wool flannel, a dress linen, and a good quality of cotton material. These were chosen with a view to uniform construction and tensile strength. Tensile strength tests were made on the Scott Cloth Tester, an average of eight breaks in each direction of the weave being taken in each case. The tests comprised washing ten times, and in the case of the cotton and linen materials, boiling ten times also. All these tests were standardized as to temperature of wash and rinse waters and method of handling. In the washing tests an initial temperature of 40° C. was used, the period of washing in the machine was ten minutes in each case, the rinsings were uniform at the same temperature, and the drying was done under controlled conditions.

For simplification, in the report which follows, the average warp breaking point is multiplied by that of the weft or filling, and the products given for comparison. Thus the breaking strength of the cotton, as purchased, was 33.25 pounds warp way, and 30 pounds filling way. The product is 997.5. After washing ten times in clear water, the removal of dressing substances brought the product down to 922.72. It is this figure with which the following comparisons are made:

Cotton washed ten times in—	
a. Clear water	922.72
b. Silicated chip soap	851.64
c. Carbonated granular soap	806.52
d. Perborate bleach soap	759.00
Linen washed ten times in—	
a. Clear water	1,514.36
b. Silicated chip soap	1,432.05
c. Carbonated granular soap	1,368.00
d. Perborate bleach soap	1,297.61

Wool washed ten times in—

a. Clear water	400.20
b. Silicated chip soap	359.70
c. Carbonated granular soap	350.20
d. Perborate bleach soap	324.94

Cotton boiled ten times in—

a. Clear water	813.58
b. Silicated chip soap	729.36
c. Carbonated granular soap	659.13
d. Perborate bleach soap	447.62

(Linen, in the following test, shows the effect of shrinkage produced by boiling. Its tensile strength increased from a product of 1,514.36 after washing ten times in clear water, to a product of 1,783.58.)

Linen boiled ten times in—

a. Clear water	1,783.58
b. Silicated chip soap	1,205.38
c. Carbonated granular soap	1,204.84
d. Perborate bleach soap	757.59

Many tests were also made to rate different soaps as to detergent power. In several of these, a standard soiled muslin has been used. This is the material recommended by the American Oil Chemists' Society, the composition of the soil being:

Wheat starch	56.82 per cent
Gum tragacanth	3.41 per cent
Edible tallow	11.36 per cent
Lampblack	17.04 per cent

The soil was printed in stripes on the muslin, the intervening stripes being left white.

The soaps used were a rosin bar soap, a silicated white bar soap, a borax bar soap, a mild flake soap, a mild chip soap, a carbonated soap, a soap containing some carbonate and some silicate, a perborate bleach soap, and a trisodium phosphate preparation. The strength of solution was 0.25 per cent, based on the bone dry soap.

The material was cut to measure and each piece washed in the same amount of solution, in a motor driven machine designed to eliminate all friction. The machine was operated with an oscillating motion at constant speed. Ten ten-minute washings were given each sample, followed by two five-minute rinsings, at the same temperature as the wash water. The initial temperature for the first run of washing tests was 40° C.; for a second set of washings on new samples, all other conditions being equal, the temperature was 80° C.

It was not planned to remove the soil entirely in these tests, but to reduce it to a comparative basis. The results were judged as to (1) the total diminution of the soil, shown by the decrease in color of the black stripes, and (2) the clearness of the white stripes, showing that such soil as had been removed from the black stripes had been floated off by the soap and not deposited again on the white part.

The temperature of 40° C. did not prove so satisfactory for the removal of this particular dirt, of which tallow, a hard fat, formed a part, as the higher temperature proved.

Those products containing less soap in proportion to building material did not remove the dirt so completely from the black stripes, and left much of the loosened dirt on the white stripes.

The depth of suds of each soap was measured in the washing machine directly after the motion ceased. The two soaps which gave the best results in cleansing were found to have the final suds equal in height, and twice as high as the soaps with alkaline builders. The two soaps which approached these first two in sudsing power were the rosin soap, three-fourths as high, and the silicated product, a little less than three-fourths. The character of the suds was slightly heavier in the lower heights.

The comparative cleanliness of the standard soiled muslin after the washing tests were completed was rated by forty-eight judges acting independently. The final results of their ratings gave first place to a pure mild soap flake and a mild chip soap, these being practically equal in rank; second place to the soap containing some carbonate and silicate; third, to a perborate bleach soap; fourth, to the rosin bar soap; fifth, a tie between a borax soap and a white naphtha soap in bar form; sixth, to the heavily carbonated product, and last place to the trisodium phosphate product, which was distinctly inferior to any of the soap products in its cleansing action.

The results of these tests would no doubt vary somewhat if obtained in different degrees of hard water, without previously softening the water. In such case the action of the soaps would differ according to the amount of water softener they contained. But when the water is softened previous to the entrance of the soap the findings should, generally speaking, be the same.

Other tests have confirmed the same conclusion: That in soft water nothing cleanses better than a concentrated pure soap, or

one with the addition of only enough builder, preferably of the colloid type, to restrain soap hydrolysis without adding materially to the alkalinity.

Comparative tests to determine the effect of certain detergents on the strength of cotton, wool, and silk fabrics are reported by the Cowles Detergent Company, of Cleveland, Ohio. Some of these tests were made in the laboratories of Arthur D. Little, Inc., Cambridge, Mass. The detergents used were solutions of soda ash, caustic soda, modified soda, and the Cowles Company's special builder product which contains a colloidal silicate, and which was mentioned as "X" in the bactericidal tests in which it was used, reported in Chapter VIII.

These tests are reported in the Cowles Company's Bulletin, *The Story of Alkali Used in Cleansing.* The first test described was made in the Little laboratory, on cotton sheeting, using as detergents 0.1 per cent solutions of soda ash and of "X." After a twenty-four hour exposure to boiling temperature in each of these solutions, the soda ash had weakened the fabric more than twice as much as the "X" in the direction of the warp threads, and one and one-half as much, as an average of fabric strength, in all directions.

Further tests, quoted from this bulletin, were as follows:

Cotton threads were immersed in solutions of two per cent strength for one hour at 180° F. There was a loss of 22.1 per cent in strength after soda ash; six per cent after modified soda; two per cent after "X." Continuing the effect of these strong solutions, twenty-five washings showed a six per cent loss with "X"; twenty-eight per cent with soda ash, and sixty-eight per cent with caustic soda. One hundred washes under the same conditions brought these respective figures to twenty-two per cent, seventy-eight per cent, and eighty-six per cent. In these washing tests the caustic soda solution was one-third as strong as the other two.

Woolen cloth boiled for twenty minutes in a 0.1 per cent solution of caustic soda, soda ash, and "X" respectively, showed complete solution with the caustic, 24.2 per cent loss with soda ash, and no loss with "X" except that which was balanced by shrinkage.

In connection with these tests on detergents of a soap nature, reference is made to the tests of penetrability of grease in fiber cells, and the action of soap in removal, reported in Chapter II.

Evaluation of Detergents

The Student's Evaluation of Detergents

What can the student do to evaluate detergents? The tests and evaluations described in this chapter may suggest simple experiments along the same lines, that can be performed by students in clothing, home management, or general science courses, even before they enter high school. With very simple apparatus, a fair estimation can be made of those detergents which the students are meeting in their homes. They can group these as to types and possible uses; distinguish between silicated and rosin soaps; test for comparative amounts of free alkali by phenolphthalein on the dry product, or its solution in alcohol; use the dilute acid test to discover carbonated soda in greater or less amounts; the tincture of turmeric test for borax; the ammonium molybdate test for phosphates; comparative sudsing, emulsification, and washing tests; the boiling test with white wool for a fair comparison of alkalinity, and so build up for themselves a working knowledge of detergents and a basis of choice for different uses.

The Home Consumer's Evaluation

What can the home consumer know? What definite attitudes and knowledges may the consumer have as she buys and uses detergents?

She may note the packaging of the article, its neatness, convenience, net contents and price, in comparison with similar products.

The advertising matter should be considered. Does it appeal to her intelligence, or does it stamp itself as unsound by too sweeping and incompatible claims?

Are the directions for use based on correct methods? If so, she will follow them as a fair test of the product.

The form of the product will help to decide its composition, adaptation to particular uses, and points of economy in quantity to be used, time saved, convenience of storage.

From a trial of the product its efficiency may be noted, possibly its effect on delicate fabrics and colors, and also—a less valid test—its effect on her hands.

She will seek a background of information on stains and their removal; textile fibers, and the effect of alkalies upon them; proper

methods of laundering special fabrics and delicate colors; the treatment of hard water; the control of temperature, and the effect of bleaches.

And realizing that with the modern trend toward finer surfaces and more costly materials, the responsibility for the conservation of these is great, and that laundering is often more destructive, when unintelligently done, than daily wear, she will do her part in conserving these materials by employing not only the right method but a wisely chosen soap.

CHAPTER XI

EDUCATIONAL ASPECTS

Relation of the School to Detergents

In the preceding chapters, the homely subject of detergents and the problems of detergency have been considered in some detail, with the purpose of showing their importance in daily life.

The Relation of Detergents to the School Curriculum

A socialized school curriculum which undertakes to train for daily living cannot omit teaching some of the subject matter relating to detergents, because of the practical values involved, values which are hygienic, economic, and scientific in nature. Starting with the little children, one of the objectives of such a curriculum is training in health habits, among these personal cleanliness and the care of clothing. With older students there will come added emphases, for with increasing interest in science the subject broadens.

It would defeat the aim of true teaching of a subject so broad in its outreachings, to dictate that in a certain month of a given grade soaps are to be studied—and then dropped. Nor can such a study be classified under one subject heading, since it belongs to hygiene, bacteriology, industrial arts, pure and applied economics, physics, and chemistry. Therefore it is far from the purpose of this chapter to recommend definite grade placements or teaching units, particularly in the elementary school. The teaching of science here, often means seizing the interest leads of the embryo chemists and physicists who are just becoming cognizant of scientific facts which challenge them to think and understand.

If most of the subject matter of the curriculum must follow a certain rigid outline, at least let the course in industrial or general science in the elementary school be fluid enough to take in anything, be it chemistry, physics, or relativity, for which the child in his awakening interest demands a scientific explanation, and which can be simplified for his present capacities. That child is

to be pitied whose eager interest is killed by "You will learn about that in high school." Yes, and often he can learn it now, because he is interested; and he may not be interested then. A certain seven-year-old boy was so thrilled by the theory of atomic structure, simply presented, about which he had inquired, that after nearly ten years it is still one of his major interests.

Science, not sciences, is what the growing child asks for. When the question comes, it is never too early to teach chemistry and physics, not as separate sciences but as tributaries to the stream of life. Analyse the waters of the stream, and physics mingles with chemistry and chemistry with biology; and so should they be taught at first, nor ever separated by the sort of textbook teaching which is bound by chapter headings. So with little children, do not be afraid to give physics if necessary, but do fear to deaden interest with cold facts, unwarmed by vital experience or imagination. Walt Whitman's astronomer ("When I heard the learned astronomer . . ."), if he had been a real teacher, might have sent him out to look at the stars with infinitely enhanced appreciation.

The Study of Detergents in Elementary Grades

Lest there should be brought an accusation of theorizing concerning the study of detergents in the elementary grades without the offer of a definite plan for converting a prosaic cake of soap into a study with interest and value, reference is made to the writer's book *Soap Bubbles* (Macmillan Company, 1929), in which this problem is met by information in story form for supplementary reading or teaching material in industrial science for the fourth or fifth grades. It is a story growing out of the questions which a group of children may ask naturally about soap and similar products; through the activities of the children the answers to many of these questions are worked out, and to the main points of interest are brought contributions from history, geography, commerce and manufacture, chemistry, physics, and practical economics. Are there not values here for daily living which do not come with the study of the habits of the three-toed sloth, for instance?

Elementary and junior high school programs to the number of some forty each have been studied to see what definite mention could be found of the study of detergents. There were com-

paratively few direct references to detergents or related subjects, unless the general topic of hygiene might be said to promise inclusion of these. In Oakland, Calif., the program for grades 1 to 5 in industrial arts includes washing clothes in the Indian fashion and comparing with modern methods. In the practical arts course in the Denver elementary schools attention is given to procedure in washing clothes, but no direct reference is made to the study of soaps. In the Chicago public schools a suggestion is made for the study of sources of soap materials and manufacture, in the program for industrial arts in grade 5. In grade 3 of the Cicero, Ill., schools is a project in home cleaning and laundering. Paterson, N. J., suggests, in the elementary schools, an experimental study in making soap and the use of soap in cleansing. In Kern County, Calif., elementary schools, care of clothing, and hard water. In the Platoon School of Newton, Iowa, grade 3, "How is soap made? What makes water hard? How can water be made soft?" In Houston, Texas, grade 6, "Water and Soap," and in the Boston schools, intermediate grades, "Washing of Clothing."

In the Junior High School

In the junior high school science courses, Denver makes a study of soap in grade 7A. New Britain, Conn., studies hard water, emulsions, surface tension; Oakland, the use of soap in hard water; in the San Francisco public schools in grade 8A, the use of soap with different fabrics. In the Pittsburgh schools, elementary science for eighth year, we find: "How is soap made? Make soap. How was it made in colonial times? What is a wool soap? Kinds of soap and reasons for using various kinds. How does soap cleanse? Care of clothing." In St. Louis, grade 8, soap is studied in connection with a study of water, and a collection of washing and scouring preparations is made. Jamestown, N. Y., makes a similar study. Also the New York State course of study for public schools includes in grade 8 work a study of the uses of water in the home and the making of soap. In Columbus, Ohio, the subject is optional in grade 8; in Lakewood, Ohio, soap and soap manufacture are included in grade 8B, and also in this grade in Kenosha, Wis. In Hackensack, N. J., the course in science for junior high schools includes a detailed study of detergents, in the shape of twenty-six problems connected with soap. In Harrisburg,

Pa., grade 8, the history of soap, kinds and action of soap, and soap-making are studied.

In Dr. Annie Robertson Dyer's study of placement of Home Economics subject matter, entitled *The Placement of Home Economics Content in Junior and Senior High Schools* (Bureau of Publications, Teachers College, Columbia University), a study which analyses the subject content of one hundred courses, by grades, soaps and related subject matter appear in the following courses:

CLOTHING

Topic: Laundering Garments, Fine Fabrics

Grades	7	8	9	10	11	12
Occurrence per 100 courses	22	31	54	44	52	52

HOUSE AND ITS CARE

Topic: Household Care and Cleaning

Grades	7	8	9	10	11	12
Occurrence per 100 courses	67	71	79	65	74	71

HEALTH AND THE HOME

Topic: Personal Health

Grades	7	8	9	10	11	12
Occurrence per 100 courses	81	72	74	69	78	64

Topic: Sanitation in the Home

Grades	7	8	9	10	11	12
Occurrence per 100 courses	31	33	45	47	78	72

Thus it appears that there may be more than one opportunity to introduce the study of detergents in the homemaking courses of the junior and senior high schools, but that there is far from a universal introduction of the important related topics of laundering, the cleaning and sanitation of the home, and personal health. And what about the girls who do not take home economics courses? What about the boys who may never meet some of these questions in general science?

Certainly some vital knowledges and appreciations which should become a part of the equipment for daily living of every girl—and also every boy—by the end of junior high school, are those connected with the care of their clothing, the maintenance of their health, and sanitation as affecting their environment. Should not the following be necessary knowledges by the end of this period of their school training?

The source, nature, and properties of textile material in order to recognize differences in fabrics, appreciate values, and understand the proper care of clothing.

The nature of dirt and common stains, the effect on textile material and the proper remedies, in order to keep clothing in good condition and prevent economic loss.

A practical knowledge of the chemical nature of detergents and their detergent action, in order to adapt both cleanser and method to a particular purpose.

The problem of hard water, a most vital one to be understood and met intelligently.

The Senior High School

Perhaps there is little opportunity for a separate study of soaps in high school courses in physics, chemistry, etc., as at present organized. But in the field of concrete illustrations of chemical and physical facts in everyday experience, detergents offer numerous opportunities. For instance, in illustrating the abstractions of chemistry, turn to soaps for evidences of the interaction of acids and bases, mass action, ionization, hydrogen ion concentration, solutions and the behavior of colloidal solutions, effect of temperature in accelerating chemical reactions, reactions in softening hard water, recognition tests for familiar ions such as the carbonate, chloride, sodium, potassium, phosphate, etc.; and also metallic substances found in scouring preparations, and relative hardness.

A physics course may get illustrative material from the physical nature of soap solutions, including surface and interfacial tension, emulsification, adsorption, sudsing power.

A history project may be early soap manufacture and the influence of soap on civilization through the ages.

In civics, a project may be home and community standards of sanitation and health, and achievement through cleanliness.

In bacteriology, a project may be the reduction of colonies of the more common bacteria through the use of soap.

So taught, these will not be, as Dewey says, "facts torn away from their original place in experience," but will be so connected with some vital experience or activity that the general truth or principle will take on life and meaning, instead of being a mere abstraction.

In Colleges or Universities

In colleges or universities the study of detergents may assume a technical nature, if the student needs such emphasis for his future work; or a practical aspect if the findings are to be translated into home judgment and use, as in the present instance. In either case, emphasis should be placed first of all on standard methods of analysis and other established evaluations. After the technique of analysis is acquired, there is always a need for analyses and evaluations of the market products as they appear, in connection also with the new types of fabric material which the textile manufacturer frequently introduces. For, in studying the cleansing efficiency of any soap product, its effect on the strength of the textile or the household surface to be cleansed must be equally emphasized.

Conclusion

Suggestions for Further Research

In a line of research tending toward the improvement of existing products, the great need in this country is for the relief of the hard water situation in small towns or isolated communities which do not have municipal softening plants. If a laundry soap can be devised, or a protective body introduced for a reasonable cost, which can be used in hard water without the formation of the slimy curd and without chemical action on clothing, it will be the greatest of blessings to the country at large. This may be attained by using oils for the soap base in order to make a special product not affected by lime, by finding some stabilizer which will effectually prevent the hydrolysis of soap and restrain the formation of lime soap, or some peptizing agent which will break up the curds into such minute particles that they will disappear in the water and will not cling to clothing. Work along these lines is being carried on with regard to textile scouring soaps, especially as to the action of hexalin and similar compounds. The day may come when research will perfect the household product also, and hard water troubles will become things of the past.

Another valuable line of research lies in the field of substituting some bases of the organic type for sodium or potassium hydroxide in the manufacture of soap. One of these which offers interesting possibilities is triethanolamine. Triethanolamine oleate has

been prepared (*Journal of Industrial and Engineering Chemistry*, Feb., 1930) which has low surface tension, high emulsifying power, and only slight ionization. It is therefore practically a neutral soap, with a pH in five per cent solution of only 7.8. Koganei (*Journal of Biochemistry*, 3, 19, 1923) was one of the early investigators of the behavior of this and similar organic bases when combined with fatty acids.

Further developments await the investigator in the field of cellulose chemistry, particularly from the detergent standpoint, in the control of bleaching agents and alkalies in the formation of oxycelluloses.

But by far the widest field of research lies in further study of colloid-chemical and colloid-physical phenomena, with all that may develop in the fuller understanding of the nature and behavior of soaps and textile material.

The bibliography which follows is recommended as a guide not only to the practical aspects of detergents, but to further study of a technical and advanced nature.

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